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905004 [redacted]

Engineering Report

PALMER STREET LANDFILL CLOSURE/POST-CLOSURE PLAN (EPA ID NYD002126910)

VOLUME II : APPENDICES

Moench Tanning Company
Division of Brown Group, Inc.
Gowanda, New York

October 4, 1985
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Project No. 0605-12-1

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PALMER STREET LANDFILL
CLOSURE/POST-CLOSURE PLAN

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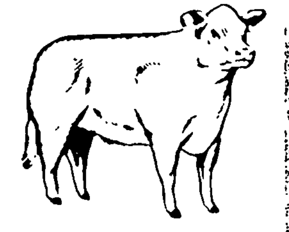
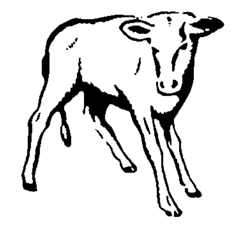
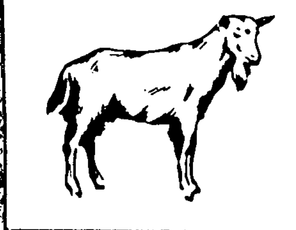
LEATHER TANNING INFORMATION



CATTLE, raised chiefly for beef, are a major source of leather. Strong, durable, flexible and capable of taking beautiful finishes and colors, cattle hides are chiefly used for shoe upper leather and sole leather. These hides are also used for luggage, upholstery, belts, wallets, clothing, and many shoe components.



CALF leather has a fine grain and a firm texture. Elegant in appearance and long wearing, calf leather is used chiefly in shoe uppers for men's and women's shoes. Other major uses include handbags and belts.



GOATSKIN and kidskin are chiefly imported from abroad. Most suedes are kidskins buffed on the flesh side. One of the sturdiest of leathers, kid is also one of the softest and most pliable. This leather, smooth or suede, is used for women's shoes, handbags and apparel.

SHEEP and lambskins are used for shoe uppers and shoe linings, slippers, garments, gloves, handbags, book bindings and other articles. Lambskins with the wool left on, called shearlings, are used for coats, jackets, boots, slippers and other cold weather garb.

Other animals in our leather zoo come from many lands and oceans. **PECCARY**, a wild hog found in South America, is our main source of pigskin for shoes, gloves, wallets, luggage. **DOMESTIC HOGS** are a source of leather for shoe uppers and gloves. **KANGAROO**, a native of Australia, provides the strongest of all leathers which is used for track and baseball shoes as well as dress shoes. **REPTILES**—snakes and lizards—from the cobras of India to the pythons of South America, provide bizarre-textured and colored leathers for shoes, bags, luggage. **BUCKSKIN** is a leather made from domestic deerskins, supplemented by skins from Canada and Latin America. Buckskin is used for leisure wear in shoes, jackets and gloves. **HORSES** provide a rugged leather which has many uses. The shell layer of the horsehide butt is tanned into cordovan leather which makes extremely supple, durable and highly polished shoe uppers. The front of the hide is used for leather jackets, baseballs and shoes. **WATER BUFFALO**, from Asia, provide strong leather for shoe uppers, luggage and handbags. **SEALSKIN** from Arctic waters is tanned for luggage and fancy leather goods such as wallets. **SHARKS**, hunted in many oceans, provide leather for shoe upppers and small leather goods.

LEATHER IN THE MODERN WORLD

LEATHER, product of an ancient craft wedded to modern science, is a 20th century miracle.

Combining raw animal skins with the most recent developments in chemical technology, American tanners are producing leather which is stronger, more attractive and more versatile in its uses.

New chemicals and modern dyes produce leathers soft and silken, sparkling like jewels and more lustrous than the rainbow. Tougher than the Roman centurion's leather shield, today's leather still guards our lives and health.

LEATHER, old as man himself, has taken on new appearances, new qualities in answer to new needs of modern man.

Primitive man used the hides of the animals he killed for food to protect his feet, power his slingshots and keep him cool in summer and warm in winter. In today's world we still wear leather shoes and leather apparel.

LEATHER, a by-product of the meat packing industry, supplies a basic raw material for a multi-billion dollar shoe industry.

Some 400 tanneries scattered across the United States produce the tens of millions of square feet of leather which provide a livelihood for tens of thousands of American workers in shoe and leather goods plants. While most of the leather produced in the United States comes from cattle raised here, millions of skins are imported annually.

LEATHER, once reserved for the powerful prince and the rich merchant, is today the common possession of every American. People everywhere love leather, but most of all young people in America love and wear it. Leather is the natural, the genuine, the real material and as such appeals to young men and women. So we see them wearing leather boots, coats, dresses and jackets to school and to jobs in offices and plants. We see young girls wearing fringed vests, carrying suede leather handbags and wearing headbands, barrettes and "chokers" of leather.

Leather keeps more than 200,000,000 Americans walking in fashion, comfort and health—in better shoes than any other people in the world. Leather jackets, coats, dresses, skirts, handbags, belts and a host of other articles are the fashion leaders of every wardrobe. Lightweight leather luggage makes travel easier. Elegant leather furniture brings beauty into the home, office, automobile. Leather is found in ball parks, stadiums, gymnasiums, golf courses—wherever America plays. Leather belting, tough but flexible, helps turn the wheels of industry.

HOW LEATHER IS MADE

Tanning is the manufacturing process by which animal hides and skins are transformed into soft, pliable leather through chemical treatments. All the leathers we use are produced through variations in the chemical processes.

Scientific control of chemical agents and tanning extracts yields the soft, supple, durable American leathers required for shoe uppers or the firmness and flexibility needed for shoe soles. Dyes and finishes applied during the tanning process produce the multitude of tones, textures and surface effects which enrich and enhance the leather used in shoes, garments, gloves, belts, luggage, handbags and the dozens of other products made of American leather.

The two principal tanning methods are chrome tanning and vegetable tanning.

Even before the hides and skins reach the tannery, they must be properly cared for. The first step after removal of hides and skins in the packing house is curing to protect the raw material until tanning is started.

PRESERVING THE HIDES

Although many hides and skins are still preserved by being spread with layers of salt, a new system is making rapid progress. In many packing plants the hides and skins are immersed in a brine solution which is circulated by pumps or agitators. The penetration of the brine preserves the hide and skin just as effectively as though it had been covered with salt for 30 days.

The first steps at the tanning plant are preliminary and include washing and soaking the hides or skins. This operation has two purposes:

First, to remove excess salt and any foreign substances; second, to restore the fibers to their natural shape and condition so that they will absorb tanning agents readily.

The next essential preparatory stage is loosening and removing the hair. Lime solutions as well as enzyme materials are used to loosen the hair from the skin. The hides and skins are then put through a dehairing machine which leaves a smooth surface with a distinctive grain pattern. A similar machine cleanses and levels the underside of the raw material.

VEGETABLE TANNING

Modern vegetable tanning uses bark and wood extracts plus chemicals to produce leather. Many trees from distant lands contribute to the basic vegetable tanning method. Among the most important are the quebracho tree of South America, the mangrove of Borneo, the valonia of Asia Minor and the gambier of India. The chestnut, oak and hemlock trees are the most important domestic sources of tanning barks. In the production of most American leather, chemicals are combined with vegetable tannins to speed the tanning period and to produce rich, lighter leathers. Most shoe soles, luggage and upholstery leathers and industrial belting are made from vegetable tanned cattle hides.

In vegetable tanning, the hides are suspended from racks or rocking frames in vats in which tanning solutions permeate the hides. The skins are moved from vat to vat, with the stronger solutions in each vat. After a time, the hides are left to soak in lay-away sections where the leather matures. After it is tanned, the leather is bleached and stuffed—that is, natural oils and greases are added in combinations of salts, oils and clay. The final product of vegetable tanning is a firm, durable and water resistant leather.

CHROME TANNING

The chrome tanning process is used in almost all plants producing leather for shoe uppers, garments and other fashion accessories. Its advantages are speed and the enrichment of leather with specific qualities which can be "built-in" during the original processing. Chrome tanning operations are completed in a matter of hours instead of weeks. Chrome tanned leather has great flexibility, gives long wear and resists scratch, scuff and scarring. For chrome tanning, lightweight cattle hides, calf, sheep, lamb, goat and pig skins are best.

During the chrome tanning process, hides and skins are tumbled in huge drums partly filled with chrome salt solutions which turns the skins a light blue-green. Then the leather is cleaned, dried and smoothed in a series of automatically controlled operations. Now the leather is ready for bleaching and dyeing. A combination of tanning methods—vegetable and chrome tanning—is sometimes used for leathers with special qualities such as glove-soft upper leather, and extremely pliable garment leathers.

Leather for shoes, garments, handbags, etc., can now be dyed in nearly 500 different colors. In conjunction with dyeing, the natural beauty of the leather is heightened through a variety of different finishes, and its fashion uses are thus extended. Among the common finishes are smooth, grained, waxy, suede, patent and lustre leather. During the tanning process some grain effects are improved through shrinking. Suede, another popular finish, is made by buffing the flesh side of the leather to raise a soft nap.

RESEARCH BY AMERICAN TANNERS IMPROVES QUALITY

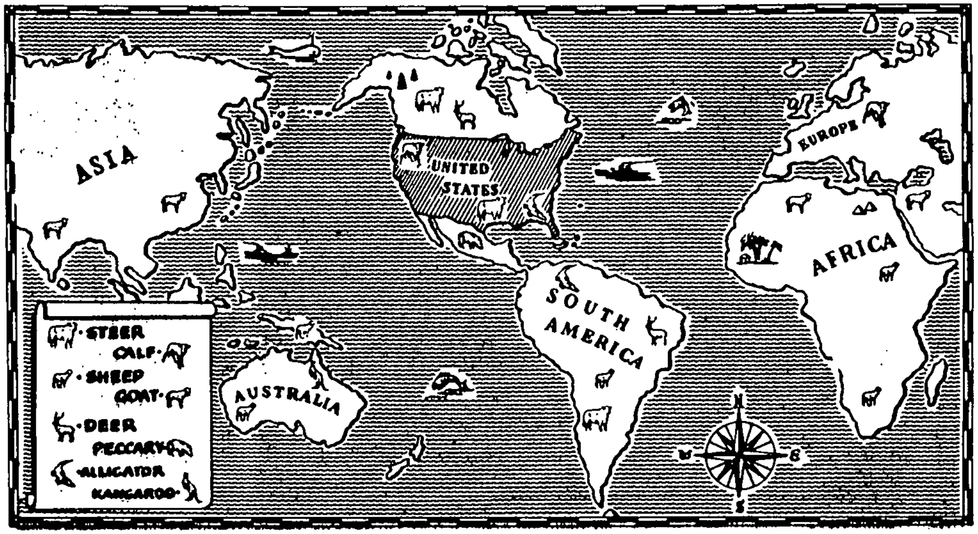
Research and engineering have been combined to improve the quality of leather, produce new varieties, finishes and colors, and to provide new products for the everyday use of the American people. Some types of leather are treated with urethane compounds to produce extremely high scuff resistance. Garment leathers are made soil-resistant through use of new fluoride chemicals which cause the leather fibers to shed oil and grease stains. Washable leathers have been developed for shoes, gloves and garments.

U.S. tanners have also adapted chemical discoveries to produce leather with unusual properties. Silicones, for example, make upper leather waterproof without hindering the leather's ability to dissipate foot moisture. Leather for white shoes, and even for baseballs, is manufactured in a process utilizing zirconium.

The U.S. tanning industry spends millions of dollars annually in research and development. Two cooperative research programs are maintained at industrial-scientific laboratories at the University of Cincinnati and the University of Wisconsin. In addition, every tannery has its own staff of chemists, engineers and technicians developing new leathers to meet new consumer needs.

The introduction of electronically-controlled equipment into American tanneries has speeded up production and trimmed costs down the line from tanner to consumer. At the same time, modern machinery has standardized the tanning and dyeing processes, producing leather of higher quality and more vibrant color.

HIDES FROM THE FOUR CORNERS OF THE WORLD

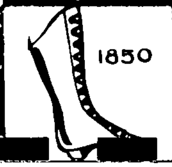


A MODERN INDUSTRY

In 1970, American tanneries processed more than 118,000,000 hides and skins. Some 44,000,000—chiefly from cattle, calves, sheep, lambs and goats—originated in the United States, accounting for most of the country's leather production.

Another 74,000,000 hides and skins came from abroad, including: Goatskins from India, South America and North Africa; sheepskins from New Zealand and South America; horsehides from Argentina, France and Belgium; pigskins from South America and Europe; reptile skins from South America and Asia. Also, a multitude of miscellaneous skins from the far-flung continents and the seven seas like kangaroo, walrus, deer, seal, shark and ostrich.

The leather and allied leather products industries employ 400,000 men and women and produce a variety of fashion, consumer and industrial products which annually add more than $6,000,000,000 to the American economy.



THE STORY OF FOOTWEAR

Man has never forgotten what he discovered by accident—that leather is the ideal material for footwear. Whether he wore open sandals or knee-high riding boots, man has always prized leather because it gave him protection, support and comfort. Leather's porosity—all the world knows that leather "breathes" naturally—has protected his health even as it contributed to his comfort.

From the simple sandals worn by the Egyptians and Greeks to the delicate, light-as-air leather evening pump of the modern woman, footwear has always held the fashion spotlight.

In ancient Rome, shoes were a sign of rank and wealth. The soldier wore simple leather sandals, the Senator a soft black leather thong boot known as a calceus, while Nero wore a calf-high campagus of leather studded with jewels.

In 14th century England under Richard II, cracowes were popular at court. They were peaked shoes sometimes two and a half feet long.

Henry VIII, history's most famous victim of the gout, had shoes made nearly a foot wide at the toe—to give him relief from pain.

In 16th century Spain and Venice, ladies clomped about on chopines—leather shoes set on wood platforms sometimes a foot high.

In the 17th century, chopines gave way in Europe to more delicate, pointed mules, slippers and dancing pumps, as well as high shoes.

By the 18th century, leather brogues were common among the poorer people on farms and in cities. Cavaliers and soldiers wore leather boots.

SHOEMAKING IN AMERICA

The history of shoemaking in the United States is closely identified with the tanning industry. The leather used in making a pair of shoes represents but 15 per cent of the retail cost. Yet progress in shoe manufacture has always been linked to new improvements in leather making. Nearly 80 per cent of all leather now produced in the United States goes into the production of shoes.

In colonial America, where life was hard and industrial progress slow, shoes were hand-made of heavy, coarse leather with a thick leather sole and a leather thong for a tie. The first shoemakers, Thomas Beard and Isaac Rickman, arrived in Massachusetts from England in 1629.

Beard, Rickman and their colonial successors traveled from home to home with a kit of tools and their supply of leather. Like cobblers all over the world, they used an awl, a curved knife, needle and wooden last. Later, some shoemakers set up shops in their own homes.

FIRST SHOE FACTORY

From these home shops developed the first factories—small one-room shops where four and five workers found jobs. The first factory where each worker completed just one step in the making of a shoe was set up in Lynn, Massachusetts early in the 19th century by John Adams Dagyar.

Until 1850, practically all steps in the shoemaking process were done by hand. After Howe's invention of the sewing machine, it was adapted to stitching shoes. Then machines were developed for cutting out soles and uppers, and cementing, nailing and vulcanizing parts of the shoe. There are now nearly 10,000 machine and tool patents for shoe making equipment.

The constant improvement of leather tanning and dyeing made possible rapid, economical machine manufacture of shoes. American shoe manufacturers now produce a vast variety of different styles, sizes, shapes for men, women and children. American shoes are superior in styling, durability and value to footwear produced anywhere else in the world.

Today, the American footwear industry produces some 600,000,000 pairs of shoes every year. The average cost of a pair of leather shoes is under $8.50—less than the equivalent of three hours of labor by the average American worker.

LEATHER THROUGH THE AGES

Leather was man's first clothing material. Man, the hunter, early found that he could cure and use for sandals and crude garments the skins of the animals he killed for food. Ages before he domesticated wool-bearing animals or learned to plant cotton and spin cloth, early man was skilled in the tanning and use of leather.

Archaeologists have found bits and pieces of leather–partly preserved leather jackets and cloaks and flagons–scattered as far and wide as ancient man wandered.

Artfully decorated leather thong sandals have been unearthed from the tombs of Egypt. Obviously, they were the prized possessions of priests and nobles from the courts of the pharoahs more than 5,000 years ago.

The bogs of Scotland have yielded up partly preserved leather garments worn by the ancestors of the present day Highlanders.

Water, grain and other household items were stored in leather containers in ancient Crete.

In Athens, 500 years before the birth of Christ, the playwright Aristophanes referred to the tanner–it was already a well-established trade.

Over the centuries leather has continued to serve mankind. As the methods of tanning and working leather improved, leather became the hallmark of luxury and wealth. In medieval Europe and later, leather boots, saddles and cloaks were worn and used exclusively by the rich and noble. Only the wealthy could afford the elaborate footwear, bejewelled capes, decorated chairs and gold-scrolled chests made of leather.

It was not until the 19th century that leather was produced for a mass market–turned into hundreds of products which are now available at modest cost to every family. The discovery of new tanning materials, the invention of new machinery and the growth of huge herds of cattle in this country were chiefly responsible for bringing this former luxury within reach of all--bettering its quality and heightening its beauty at the same time.

HISTORY OF TANNING IN THE UNITED STATES

Tanning in America goes back to the days before European settlers landed on these shores. The Indians made a crude form of leather from deerskins—for their moccasins, cloaks and tents. The white man soon adapted and refined the deer and buckskin tannages. Leather became one of the most common and widely used materials in the new land. Famous frontiersmen like Daniel Boone, Davy Crockett and Jim Bowie dressed in supple deerskin shoes, pants and shirts.

The first tanner set up in business in the colonies in 1623. Experience Miller, the leather maker, came to Plymouth barely three years behind the first Pilgrims.

The first machine used in tanning in this country was invented by Peter Minuit, one of the founders and governor of New Amsterdam. His horse-driven stone mill ground oak bark, a basic tanning material.

A scientific discovery in England more than a century later was responsible for giving the United States a leading world position in tanning. Sir Humphrey Davy, the famous scientist, discovered that many other trees beside the oak could supply tanning barks. Among the new sources of tanning agents were the hemlock, chestnut and mimosa—all plentiful in the forests of the New World.

MECHANIZATION BEGINS

In 1809 another invention, this time by an American named Samuel Parker, put the tanning industry on the road to mechanization. Parker invented a machine to split heavy hides and produce leather for lighter, more supple, more comfortable shoes and boots. Formerly, a workman could laboriously split four hides a day. Using Parker's equipment, he could split 100 hides. Passing on this saving in labor costs helped bring shoes within the reach of more people.

The discovery of chrome tanning—in which mineral salts replace bark tanning agents—was another important step forward. Ever more flexible and beautiful leathers could be made for shoe uppers. Soon a large variety of chemicals were drafted into the tanneries—helping expand the American chemical industry even as it saved the nation's forest resources. Today chemists and tanners are teamed to produce leather with deep, lasting colors, handsome textures,greater durability.

As the American standard of living rose and more cattle were consumed for meat, more hides became available for tanning. Better and less expensive leather products could now be made for the mass market.

LEATHER FOR FOOT HEALTH

When man first looked around for something to shield his feet from the hardships of the elements and the many dangers in the forest and the desert, he found that animal skins offered the most protection and, in fact, were about the only long-wearing material available.

Today, modern man, who has all the resources of science and technology at hand, still uses animal skin to protect and adorn his feet —although today's leathers are a far cry from the raw hides used by our prehistoric ancestors.

Leather today is a skillful blend of the natural animal skin and the latest advances in technology. The end result is the most comfortable and healthful shoe material ever devised.

Viewed under a microscope, leather shows up not as a dense mass, but as a fine network of millions of tiny fibers linked together in a structure that no laboratory can duplicate, except nature's own.

LEATHER BREATHES

Leather can breathe because its fibrous structure permits a steady movement of air and water vapor. That is why all-leather shoes insulate the feet—keeping them warm and dry in winter and cool and dry in summer. Foot perspiration is evaporated through leather's invisible pores.

Leather shoes help guard against athlete's foot because the evaporation of foot moisture prevents the existence inside the shoe of damp heat in which thrive the athlete's foot fungus and similar bacteria and germs.

Sometimes our youngsters are exposed to another foot danger. This arises from wearing shoes of plastic—frequently made to look like real leather. Lacking leather's natural structure, these shoes trap heat and moisture in the shoe. Soon the moving foot is chafed and irritated. It easily falls prey to skin disease. Another problem that plastic materials pose is that they will not conform to the shape of the foot, as leather does.

DOCTORS ADVISE LEATHER SHOES

For this reason, foot doctors recommend all-leather shoes. In addition, they say, the resilient fibers in leather make possible sturdy soles which give proper support to feet and soft and supple shoe uppers which permit the feet to move freely and to expand normally.

Particularly important with young people is protection of the feet against tetanus and other infections from nails, sharp rocks and projecting pieces of glass. Scientific tests have established that leather is four times as resistant to punctures as any other shoe material.

The foot, with its 26 bones, and its multitude of muscles, nerves, blood vessels, is one of the most intricate parts in the human body. If it is to work smoothly, it requires at least a minimum of care. Following these basic rules can help guarantee healthy feet.

FIT SHOES CAREFULLY

Shoes should be carefully fitted. They should fit snugly around the heel and provide ample toe room. The tip of the shoe should be at least one-half inch away from the big toe. Leather shoes made in the U.S. are manufactured in many more sizes than elsewhere in the world, making American leather shoes the finest and most healthful for tender, growing feet.

Children should never wear "hand-me-down" shoes. One of the chief virtues of leather shoes is that leather permits the shoe to mold itself to the true shape of the foot, thus providing maximum comfort and support. Since no two feet are exactly the same—even though they are the same size—forcing a child's foot into a shoe molded by a previous wearer will cause trouble.

Parents should make sure that children do not wear sneakers and flimsy sport shoes except for sports played on soft surfaces.

When play period is over, children should change back immediately to their leather shoes. For feet's sake, children should never wear shoes of plastic.

STAHL

Approximate Pounds of V.O.C.'s Received by Moench Tanning from Stahl Finish in 1984

Substance	Approx. Pounds
Alcohols	
Butanol Normal	5,000
Diacetone Alcohol	600
Ethanol	92,000
Isopropyl Alcohol	18,000
Normal Propyl Alcohol	9,200
Alkyl Amide	
Dimethyl Formamide	600
Cyclic Amide	
n- Methylpyrrolidone	3,300
Esters	
2- Butoxyethanol Acetate	1,700
n- Butyl Acetate	2,500
2- Ethoxyethanol Acetate	18,000
2- Ethylhexyl Acetate	600
Isobutyl Acetate	170,000
2- Methoxyethanol Acetate	300

Substance	Approx. Pounds
Glycol Ethers	
2- Butoxyethanal	38,000
Butyl Carbitol	500
2- Ethoxyethanol	24,000
2- Isopropoxy Ethanol	35,000
2- Methoxy Ethanol	90,000
Propylene Glycol Methyl Ether	500
Hydrocarbon	
Mineral Sprits	900
Solvent Naphtha (Petroleum) Lt. Arom.	25,000
Stoddard Solvent	1,000
Toluene	11,000
Xylene	165,000
Ketones	
Diisobutyl Ketone	2,100
Isophorone	100
Methyl Amyl Ketone	1,800
Methyl Ethyl Ketone	3,200
Methyl Isobutyl Ketone	7,500

720 [illegible]

Substance	Approx. Pounds
Other	
Ammonium Hydroxide	5,400
Amorphous Silica	4,200
Carbon Black	2,100
Cellulose Nitrate	3,800
Chromium as Lead Chromate	900
Crystalline Silica	1,600
Dioctyl Phthalate	4,100
Lead as Lead Chromate	900
Lead as Molybdate Sulfate Chromate	1,500
Monoethanolamine	600
Morpholine	1,000
Phenol	400
Titanium Dioxide	70,000
Triethylamine	900

STAHL FINISH

BEATRICE CHEMICAL
DIV. OF BEATRICE FOODS CO.

February 7, 1984

Mr. Henk Duwe
Moench Tanning Co., Inc.
Beech & Palmer Streets
Box 389
Gowanda, N.Y. 14070

Dear Mr. Duwe:

Attached is the information on certain constituents contained in Stahl Finish products and their respective usages by Moench Tanning for the 1983 calendar year.

We have included in this tabulation all constituents that contribute to V.O.C. content, as well as other constituents that may sometimes be considered to be "hazardous".

Sales figures were only available for ten months (March-December), so we took the liberty of extrapolating sales figures for the additional two months. These calculations provided us with an approximate number of pounds of each product purchased by Moench Tanning from Stahl Finish for the 1983 calendar year. Based on these estimated annual sales figures, we determined the approximate number of pounds of each component contained within the products (Table I).

I have also enclosed Material Safety Data Sheets on those products listed in Table 2.

Do not hesitate to contact me if any additional information is needed.

Sincerely,

STAHL FINISH

Ronald P. Blanchette

Ronald P. Blanchette
Safety & Environmental
Administrator

RPB/as
Enclosures

cc: JO MG
EFB LI

36 Howley Street, Peabody, Massachusetts 01960 • Tel (617) 531-0371

MONTREAL, P. Q. WAALWIJK, NETHERLANDS LOUGHBOROUGH, ENGLAND PARETS, SPAIN
MANAGUA, NICARAGUA MEXICO CITY, MEXICO
RIO DE JANEIRO BRAZIL CAGUA, VENEZUELA SYDNEY, AUSTRALIA

TABLE I

APPROXIMATE NUMBER OF POUNDS OF RAW MATERIALS IN STAHL FINISH PRODUCTS USED BY MOENCH TANNING IN 1983 CALENDAR YEAR.

RAW MATERIALS:	POUNDS:
Solvents:	
Aromatic 100	11,500
Butanol Normal	11,500
Butyl Acetate	6,000
Butyl Cellosolve	25,000
C.D.A.	118,500
Cellosolve Acetate	28,500
Cellosolve Solvent	92,500
Diacetone Alcohol	9,000
D.I.B.K.	6,500
Hydro Carbon BP311-345	28,500
IPA	103,000
Isobutyl Acetate	313,000
Isophorone	500
Isopropyl Acetate	500
Isopropyl Cellosolve	172,000
MAK	2,500
MEK	8,500
Methyl Cellosolve	76,500
Methyl Cellosolve Acetate	500
MIBK	11,000
Mineral Spirits	1,500
M-Pyrol	1,500
NPA	62,000
Stoddard Solvent	1,000
Toluene	20,500
VM&P Naptha	1,000
Xylene	293,000
2-Ethyl Hexyl Acetate	1,000

RAW MATERIALS:	POUNDS:
Non-Solvents:	
Ammonia	6,500
Amorphous Silica	5,500
Carbon Black	5,500
Cellulose Nitrate	6,500
Crystalline Silica	1,500
DOP	3,000
MEA	1,500
Morpholine	1,000
Phenol Sol. 90% Tech.	500
Titanium Dioxide	64,500
Triethylamine	1,000

1,407,000 LBS. VOC

201,000 GAL. VOC

1.6 PRODUCTION FACTOR
8 HR DAY SPRAY
MACHINE UTILIZATION

~~M. RAWAN~~

H. DOWE

July 31, 1981

Mr. Albert Latour
Brown Shoe Co., Inc.
8300 Maryland Ave.
St. Louis, Missouri 63105

Dear Mr. Latour,

As discussed in our phone conversation, we have tabulated the quantities of solvents emitted at Moench Tanning for an entire year. The day to day composition of the solvents emitted varies but these figures probably give a better overall picture of the nature of the solvents.

I have broken the categories down into the different chemical classes. The total annual volume of solvent used is about 120,000 gallons at an average gallon weight of 7.0 lbs./gallon. This is close to 840,000 lbs./year.

KETONES

Name	Annual Vol. (Gals.)	% of Total (by vol.)
Acetone	12,600	11.3%
Diacetone Alcohol	360	0.3%
Diisoamyl Ketone	50	0.04%
Diisobutyl Ketone	770	0.7%
Isophorone	40	0.04%
Methyl Isobutyl Ketone	1,600	1.4%
Methyl Hexyl Ketone	40	0.04%
		13.8%

The ketones comprise 13.8% of the total volume of emitted solvent.

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MANAGUA NICARAGUA MEXICO CITY, MEXICO
RIO DE JANEIRO BRAZIL CARACAS VENEZUELA SYDNEY, AUSTRALIA

ESTERS

Name	Annual Vol. (gals.)	% of Total (by vol.)
Butyl Acetate	13,800	12.3%
Butyl Formate	770	0.7%
Cellosolve Acetate	1,300	1.2%
Ethyl Hexyl Acetate	140	0.1%
Ethyl Propionate	580	0.5%
Ethyl Butyrate	260	0.2%
Butyl Propionate	60	0.06%
Methyl N-Butyrate	960	0.9%
Propyl Acetate	960	0.9%
Propyl Propionate	130	0.1%
		17.0%

The esters comprise 17.0% of the total.

ALCOHOLS

Butyl Alcohol	1,370	1.2%
Denatured Ethanol	5,000	4.5%
Isopropyl Alcohol	12,100	10.7%
N-Propanol	4,100	3.7%
		20.1%

The alcohols comprise 20.1% of the total solvent.

GLYCOL ETHERS

Name	Annual Vol. (gals)	% of Total (by vol.)
Ethylene Glycol Monoethyl Ether	11,300	10.1%
Ethylene Glycol Monoisopropyl Ether	8,500	7.6%
Ethylene Glycol Monobutyl Ether	4,000	3.6%
Ethylene Glycol Monomethyl Ether	4,600	4.1%
		25.4%

The glycol ethers comprise 25.4% of the total.

HYDROCARBONS

Aromatic 100	6,000	5.4%
Stoddard Solvent	100	0.1%
Toluene	900	0.8%
Xylene	19,400	17.4%
		23.7%

The hydrocarbons comprise 23.7% of the total.

I have placed all of the isomers together except for propanol. If you need the breakdown of the specific isomers, I will get it to you.

As you can see, we use a wide variety of the commercially available solvents. We do not use nitroparaffins, halogenated hydrocarbons or aliphatic hydrocarbons. If these turn up in the complaining county, then the cause of the problem is not Moench Tanning.

STAHL FINISH

BEATRICE CHEMICAL
DIV. OF BEATRICE FOODS CO.

December 22, 1980

Mr. Henk Duwe
Moench Tanning Co., Inc.
Beech & Palmer Sts.
Box 389
Gowanda, N.Y. 14070

Dear Mr. Duwe,

Enclosed is information that I trust will be useful to you in your air pollution calculations.

To list CAS numbers for major constituents would prove to be very difficult. Additionally, since our products do not have CAS numbers, the information would probably be of little use. For those reasons I have not attemtpted to list such numbers at this time.

Please let me know if you need additional information.

1. Aqueous Pigment Dispersions

Approx. % Volatile Organic Compounds (VOC) - None
Approx. % Water -- 65-70
Approx. % Total Non-volatile (Solids) - 30-35
Total annual Purchases - 16000 gal.
Major Non-volatile constituents: Titanium Dioxide
Carbon Black
Iron Oxide
Lead Chromate
Lead Molybdate
Organic Pigments
Casein
Synthetic Resins

Products included in this category: P-8-2, SAC-11, SAC-06, SAC-40, SAC-71, SAC-72, SAC-80, SAC-86, SAC-82, 1735, 7125, 2011-NP, 2082-NP, 2083-NP, 2089-NP, 2359, 4503, P-5717.

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MANAGUA, NICARAGUA MEXICO CITY, MEXICO
RIO de JANEIRO, BRAZIL CAGUA, VENEZUELA SYDNEY, AUSTRALIA

2. Synthetic Resin Aqueous Emulsions:

Approx. % Volatile Organic Compounds (VOC) - None*
Approx % Water - 60
Approx. % total Non-volatile (Solids) - 40
Total Annual Purchases 33,000 gal.
Major Non-volatile constituents: Acrylic Polymers

Products included in this category: JL-2-P, RI-22, 115, 193, P-241, RB-241, SL-333, 666, RA-812, RI-6582, 7305, 7420, 9611, MS-2170, 993, 996, 996-A, RI-1122, 2354, 2357, RU-3904, RU-4612, RU-676

*The only significant exception is 2354, which contains about 11% VOC.

3A. Lacquers-Solvent Dilutable

Approx. % Volatile Organic Compounds (VOC) - 80-90
Approx % Water - 0-10
Approx. % Total Non-volatile (Solids) - 10-20
Total Annual Purchases - 50000 gal.
Major Volatile Constituents: Ketones
Hydrocarbons
Esters
Glycol Ethers
Alcohols
Major Non-volatile Constituents: Nitrocellulose
Cellulose Acetate butyrate
Plasticizers
Urethanes

Products included in this category: LS-1240, CR-4884-D, CR-4885-D, CR-4886-D, LS-8237, LS-8400, LS-8412, LS-8415, LS-8409, LS-8437, LS-8484, LS-585-HS, LS-1185, 21-360, 21-361, 21-362, 21-363, 21,-366, 893, CR-4882-D, LS-7245, LS-979, LSU-1002, LS-1004, LS-1071, CR-4883-D, LSU-1082, CR-4887-D, LSU-942, 25 Yellow, LS-127, LS-201-R, LS-231, LS-231-D, LS-256, LS-3493, LS-407, LS-409, LS-477, LS-801.

3B. Lacquers - Water Dilutable

Approx. % Volatile Organic Compounds (VOC) - 45-55
Approx. % Water - 25-35
Approx. % Total Non-volatile (Solids) - 10-20
Total Annual Purchases - 4400 gal.

Major Volatile Constituents: Ketones
Hydro carbons
Esters
Glycol Ethers
Alcohols
Water

Major Non-Volatile Constituents: Nitrocellulose
Cellulose Acetate butyrate
Plasticizers
Surfactants

Products included in this category: LW-5344-A, LW-5344-C, LW-88, LW-16-A, LW-93, LW-356, LW-453, LW-475, LW-620.

4. Solvent Dyes & Specialties

Approx. % Volatile Organic Compounds (VOC) - 90
Approx. % Water 0
Approx. % Total Non-volatile (Solids) - 10
Total Annual Purchases - 84,000 gal.
Major Volatile Constituents: Ketones
Hydrocarbons
Esters
Alcohols
Glycol Ethers

Major Non-volatile Constituents: Metalized Azo Dyes
Urethanes

Products included in this category: T-13, WU-2501, T-40, T-53, T-32, 87-XX, 88-XX, 90-XX, 91-XX, 92-XX, 95-XX, 94-XX, T-122, 3103, RU-3506, R4-31-5, T-6000, 45-904, HM-646, 6884, CR-691-A, CR-691-B, D-1189, LS-1100, T-1942, T-13-M, DL-2227, DL-2241, SD-115, SD-182, SD-183, SD-185, SD-186, SD-187, SD-189, SW-501, SD-275, SD-22, D-358, DL-2238, SD-402, S-435, S-426.

5. Water Specialty Finishing Products

Approx. % Volatile Organic Compounds (VOC) - * None
Approx. % Water - 80-90
Approx. % Total Non-volatile (Solids) - 10-20
Total Annual Purchases - 47,000 gal.
Major Volatile Constituents: Water

Major Non-Volatile Constituents: Clays
Waxes
Thickeners
Oils
Organic Binders
Surfactants

Products included in this category: FI-20, B-50, R-50-W, RK-630, B-150, BI-727, 168, 6972, 22-089-C, MS-947, MS-987, 71-261-M, 72-338, 95-421, EX-1690, HM-270, 4260, 5244, PT-6507, 7445, SP-9109, 281, 415, 434, 501, D-550, BI-500, RK-620, RK-637, RK-676, PT-755, L-801, MS-987.

* The only significant exceptions are 4260, PT-6507, 434, 501 and PT-755, which contain 25-40% VOC, consisting of alcohols, glycol ethers, and hydrocarbons.

Sincerely,

STAHL FINISH

Steve Ossoff

Steven B. Ossoff
Safety Director

SBO/ju

Now IN USE

Product Data

December 1, 1981

Bulletin No. D20W

Busan® 30L

(Patents issued or pending in the U.S.A. and other countries)

For Microorganism Control in Tanneries

Busan 30L is an effective and economical microbicide for preventing fungal attack of skins and hides during tannery processing and subsequent storage. It is specifically recommended for use in chrome tanning to prevent leather damage and consequent losses caused by microorganisms.

PRODUCT CHARACTERISTICS

Busan 30L is a liquid that disperses readily in water. It is packed in nonreturnable drums with bungs. Type 316 stainless steel, molded nylon, Penton, Teflon, polyethylene, and polypropylene are all satisfactory for handling Busan 30L. The composition and some of the physical properties of Busan 30L are as follows:

Active ingredient:	
2-(Thiocyanomethylthio) benzothiazole	30%
Inert ingredients	70%
Density at 25 °C (77 °F)	1.08 g/mL
Approximate weight per gallon	9.0 lb
Approximate volume per kilogram	927 mL
Approximate volume per pound	420 mL
Flashpoint by Tagliabue closed cup method	60.6 °C (123 °F)
pH of 100 parts per million in distilled water	6-7

Busan 30L is moderately toxic by ingestion in single doses and by single skin applications. The undiluted product is irritating to the skin and to the eyes. Workmen handling the product should use rubber gloves and goggles and should observe other precautions shown on the label.

APPLICATION

Because of the moist condition and acid pH of the stock, chrome-tanned stock held "in the blue" readily molds and may become discolored. Severe mold growth at this stage will usually cause permanently discolored areas that influence subsequent finishing operations and reduce the value of the leather. Treatment with Busan 30L, however, is expected to help eliminate mold growth on chrome-tanned stock when used along with good sanitation procedures.

Busan 30L should be applied as a dispersion in water. Satisfactory dispersions using one (1) part Busan 30L and three (3) parts water can be prepared with proper addition sequence and sufficient agitation. Busan 30L should be added to the water as opposed to the water being added to Busan 30L.

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MEMPHIS, TENNESSEE 38108, U.S.A.

BUCKMAN LABORATORIES PTY. LTD.
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BUCKMAN LABORATORIES, S.A.
GHENT, BELGIUM

BUCKMAN LABORATORIOS, LTDA
CAMPINAS, S.P., BRAZIL

BUCKMAN LABORATORIES OF CANADA, LTD
MONTREAL, P.Q., CANADA

BUCKMAN LABORATORIES, LTD
TOKYO, JAPAN

BUCKMAN LABORATORIES, S.A. DE C.V.
MEXICO, D.F., MEXICO

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Higher dilutions such as one (1) part Busan 30L to 19 or more parts of water are preferred where such dilutions can be conveniently used in the tanning process. Dispersions of Busan 30L in water remain stable for only a short period of time. It is thus recommended that such dispersions be prepared immediately prior to their addition to the tanning process.

Busan 30L is absorbed on the hide and therefore dispersions of Busan 30L in water must be added in a manner to insure maximum uniform distribution over the entire skin or hide. The preferred points of addition are to the pickling liquor or chrome-tanning liquor. When added to the pickling liquor, it is very important that the additions be made following neutralization of any residual lime or alkaline salts with the acid pickling liquor. Under no circumstances should Busan 30L be added to solutions or hides when the pH is above 8.0.

Under some circumstances it may be advantageous to make split additions of the Busan 30L dispersion with approximately one-half added to the pickling liquor and the remainder to the tanning liquor.

An alternate addition procedure would be to add approximately one-half of the required amount of Busan 30L dispersion to the tanning drum or vat as the initial tanning liquor charge is made. The remainder of the dispersion can then be added directly to the drum or vat with vigorous mixing just after mid-point of the tanning cycle has been completed.

Suggested treatment rates are 0.25 to 2.0 kg of Busan 30L per metric tonne (0.25 lb to 2.0 lb per 1000 lb) of white stock weight. Treatment rates will vary depending on factors such as relative fat content of the skins or hides, thickness or density of the stock, subsequent washing, neutralizing, chemical fixing agents, and the degree of preservation required for specific storage conditions. The higher treatment rates are required where the skins or hides have high fat content; where the hides are unusually thick or dense; and where final post-tanning operations such as washing, neutralizing, and chemical fixing would contribute to the extraction of Busan 30L from the hides.

When long term preservation of splits of whole hides is required, it is suggested that a supplemental surface application of the Busan 30L be made to all surfaces. This can be done by a surface spray, a vat or drum soak, or a roll/wringer application procedure. The important factor is uniform distribution of the Busan 30L dispersion onto the top and bottom surfaces of each split.

Under certain storage and/or transportation environments where long term preservation is required, the inhibition of mold growth is assisted by spraying a 1.0 percent dispersion of Busan 30L on hides or splits prior to palletizing, wrapping, or containerizing the loaded pallets. The spray application should be applied to the point of "run-off" of the dispersion from the stock surfaces. It is again important to provide uniform coverage of the sprayed surfaces with the Busan 30L dispersion.

The exact procedure for adding Busan 30L and contact time needed to provide maximum protection of hides from microbial attacks will vary from one tannery to another. The most effective program should be developed specifically for each location.

Printed in U.S.A.

DISCONTINUED

PRODUCT DATA

March 1, 1973

BUSAN® 93

(Patents issued or pending in the U.S.A. and other countries)

NEW COMBINATION MICROBICIDE FOR INDUSTRY

Busan 93 is a new industrial microbicide that combines the broad-spectrum activity of the widely-used and time-tested organobromine compound 2-bromo-4'-hydroxyacetophenone with the outstanding fungicidal properties of 2-(thiocyanomethylthio)benzothiazole. The latter compound has proven itself as an effective, nonmetallic replacement for mercurial fungicides in a number of agricultural and industrial applications. Busan 93 thus provides a wider range of activity and more efficient control of bacterial and fungal slime in pulp and paper mills.

Busan 93 is composed of substances that have been allowed for use in the manufacture of paper and paperboard under U.S. Food and Drug Administration Regulation 121.2505.

PRODUCT CHARACTERISTICS

Busan 93 is a liquid packed in 230-kg. (505-lb.) net weight, lined, nonreturnable steel drums with bungs. Penton, Teflon, polyethylene, polypropylene, molded nylon, and Type 316 stainless steel are all satisfactory for storing and handling Busan 93. The composition and some of the physical properties of Busan 93 are as follows:

Active ingredients	28 percent
★ 2-Bromo-4'-hydroxyacetophenone	20 percent
2-(Thiocyanomethylthio)benzothiazole	8 percent
Inert ingredients	72 percent
Density at 25° C. (77° F.)	1.14 g. per ml.
Approximate weight per U.S. gallon	9.5 lb.
Approximate volume per kilogram	880 ml.
Approximate volume per pound	400 ml.
Flashpoint by Tagliabue open-cup method	62° C. (144° F.)
pH of 100 parts per million in distilled water	7–8

Busan 93 is moderately toxic by ingestion in single doses and by single skin applications. The undiluted product is severely irritating to the skin and eyes. Workmen handling the product should wear rubber gloves and goggles and should observe other precautions shown on the label.

This product is toxic to fish. Treated effluent should not be discharged where it will drain into lakes, streams, ponds, or public water. Do not contaminate water by cleaning of equipment or disposal of wastes. Apply this product only as specified in this bulletin.

★ Structures on back of sheet

Buckman Laboratories, Inc.

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BUCKMAN LABORATORIES (PTY) LTD
DURBAN, SOUTH AFRICA

CREATIVITY FOR OUR CUSTOMERS

WATER TREATMENT CHEMICALS

No. NAME

Busan 93

A. Active Ingredients

1. 2-(Thiocyanomethylthio)benzothiazole (TCMTB)
2. 2-Bromo-4'-hydroxyacetophenone (BHAP)
3.

B. Recommended Dosage

0.4 - 0.5 lb. per 1000 lb. of white weight stock

C. Purpose (slimicide, scale inhibitor, etc.)

Fungicide, bactericide

D. File References (User's Name, location, SPDES number and dates of memos setting limits)

E. Recommended Criteria

Ingredient	Aquatic Standard (ppb) Non-trout	Aquatic Standard (ppb) Trout	Drinking Water (ppb)

F. Comments (detection limits, restrictions on usage, etc.)

Detection limit - 0.1 part per million for both active ingredients
Biodegradable half-life (TCMTB) - 2 hours
Biodegradable half-life (BHAP) - 100% hydrolyzed at pH 8, 30° C. in 24 hours

PRODUCT DATA

June 30, 1973

Bulletin No. D2

BUSAN® 72

(Patents issued or pending in the U.S.A. and other countries)

A MICROBICIDE FOR THE LEATHER INDUSTRY

Busan 72 is an effective and economical nonmercurial microbicide for use in preventing fungal attack of skins and hides during tannery processing. It is specifically recommended for use in chrome tanning to prevent the leather damage and consequent losses caused by these microorganisms.

The U.S. Department of Agriculture Animal and Plant Health Inspection Service has stated that Busan 72 is chemically acceptable for the treatment of skins and hides during tannery processing to control microbiological growth in official establishments operating under the Federal meat and poultry products inspection program. This product must be used in a manner which precludes contact with edible meat or poultry products.

PRODUCT CHARACTERISTICS

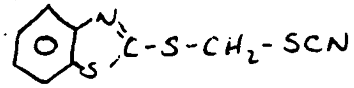
Busan 72 is an emulsifiable liquid packed in 250-kg. (550-lb.) net weight, lined, nonreturnable steel drums with bungs. Type 316 stainless steel, molded nylon, Penton, Teflon, polyethylene, and polypropylene are all satisfactory for handling Busan 72. The composition and some of the physical properties of Busan 72 are as follows:

Active ingredient:	
2-(Thiocyanomethylthio)benzothiazole	60 percent
Inert ingredients	40 percent
Density at 25° C. (77° F.)	1.24 g. per ml.
Approximate weight per U.S. gallon	10.3 lb.
Approximate volume per kilogram	805 ml.
Approximate volume per pound	365 ml.
Flashpoint by Tagliabue open-cup method	Above 120° C. (248° F.)
pH of 100 parts per million in distilled water	5–6

Busan 72 is moderately toxic by ingestion in single doses and by single skin applications. The undiluted product is severely irritating to the skin and is corrosive to the eyes. Workmen handling the product should use rubber gloves and goggles and should observe other precautions shown on the label.

This product is toxic to fish. Keep out of lakes, streams, or ponds. Do not contaminate water by cleaning of equipment, or disposal of wastes. Apply this product only as specified on the label.

2-(Thiocyanomethylthio)benzothiazole



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BUCKMAN LABORATORIES (PTY) LTD
DURBAN SOUTH AFRICA

CREATIVITY FOR OUR CUSTOMERS

WATER TREATMENT CHEMICALS

No.	NAME
	Busan 72

A. Active Ingredients

1. 2-(Thiocyanomethylthio)benzothiazole (TCMTB)
2.
3.

B. Recommended Dosage

0.2 - 0.3 lb. per 1000 lb. white weight stock

C. Purpose (slimicide, scale inhibitor, etc.)

Fungicide

D. File References (User's Name, location, SPDES number and dates of memos setting limits)

E. Recommended Criteria

Ingredient	Aquatic Standard (ppb)		Drinking Water (ppb)
	Non-trout	Trout	

F. Comments (detection limits, restrictions on usage, etc.)

Detection limit - 0.1 part per million
Biodegradable half-life - 2 hours in paper mill waste treatment

Form G-1 4/78

CONFIDENTIAL

MATERIAL SAFETY DATA SHEET

● Section 1 – PRODUCT IDENTIFICATION

MANUFACTURER'S NAME
DEARBORN CHEMICAL (U.S.), CHEMED CORPORATION .

EMERGENCY PHONE NO.
312/438-8241

ADDRESS
300 Genesee St., Lake Zurich, IL 60047

CHEMICAL NAME AND SYNONYMS
Boiler water treatment

TRADE NAME OR CODE IDENT.
SLUDGTROL® 600

● Section 2 – INGREDIENTS

	CAS No.	%	EXPOSURE CRITERIA

STYRENE SULFONATE COPOLYMER, 10% ACTIVE, AQUEOUS SOLUTION

NON-HAZARDOUS MATERIAL

The product identified in this Data Sheet is NOT a hazardous material within the meaning of Title 29, Code of Federal Regulations 1915, 1916, 1917.

● Section 3 – PHYSICAL DATA

BOILING POINT, 760mm Hg approx	212° F.	MELTING POINT	
SPECIFIC GRAVITY (H_2O = 1)	1.03	VAPOR PRESSURE	
VAPOR DENSITY (AIR = 1)		SOLUBILITY IN H_2O, % BY WT.	Complete
% VOLATILES BY VOLUME		EVAPORATION RATE, ______ = 1	
APPEARANCE AND ODOR Brown liquid		pH	9.2

● Section 4 – FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (and Method Used) None	FLAMMABLE LIMITS in AIR, % by VOLUME LOWER UPPER	AUTO IGNITION TEMPERATURE

EXTINGUISHING MEDIA ☐ Water Fog ☐ Foam ☐ CO_2 ☐ Dry Chemical ☐ Other

SPECIAL FIRE FIGHTING PROCEDURES

UNUSUAL FIRE AND EXPLOSION HAZARD

● Section 5 – REACTIVITY DATA

STABILITY (Normal Conditions)
☒ Stable ☐ Unstable

CONDITIONS TO AVOID

INCOMPATIBILITY (Materials to Avoid)
With strong acid and oxidizing material

HAZARDOUS DECOMPOSITION PRODUCTS

HAZARDOUS POLYMERIZATION
☐ May Occur ☒ Will Not Occur

CONDITIONS TO AVOID

(over)

[redacted]

MATERIAL SAFETY DATA SHEET

• Section 1 – PRODUCT IDENTIFICATION

MANUFACTURER'S NAME DEARBORN CHEMICAL CO., Subsidiary, W. R. Grace & Co.	EMERGENCY PHONE NO. 312/438-8241
ADDRESS 300 Genesee St., Lake Zurich, IL 60047	
CHEMICAL NAME AND SYNONYMS Return line treatment	TRADE NAME OR CODE IDENT. STEAMATE®2001

• Section 2 – INGREDIENTS

INGREDIENTS	CAS No.	%	EXPOSURE CRITERIA
Cyclohexylamine)	108-91-8	approx. 30	TWA: 10 ppm (skin)
Diethylaminoethanol)	100-37-8		TWA: 10 ppm (skin)
Morpholine)	110-91-8		TWA: 20 ppm (skin)

• Section 3 – PHYSICAL DATA

BOILING POINT, 760mm Hg approx.	210°F.	MELTING POINT	
SPECIFIC GRAVITY (H_2O = 1)	0.99	VAPOR PRESSURE	
VAPOR DENSITY (AIR = 1)		SOLUBILITY IN H_2O, % BY WT.	Complete
% VOLATILES BY VOLUME	100	EVAPORATION RATE, ________ = 1	
APPEARANCE AND ODOR Yellow liquid, amine odor		pH	13.1

• Section 4 – FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (and Method Used)	FLAMMABLE LIMITS in AIR, % by VOLUME LOWER UPPER	AUTO IGNITION TEMPERATURE
135° F. Tag CC		

EXTINGUISHING MEDIA ☐ Water Fog ☒ Foam ☒ CO_2 ☐ Dry Chemical ☐ Other

SPECIAL FIRE FIGHTING PROCEDURES

UNUSUAL FIRE AND EXPLOSION HAZARD

• Section 5 – REACTIVITY DATA

STABILITY (Normal Conditions) ☒ Stable ☐ Unstable	CONDITIONS TO AVOID
INCOMPATIBILITY (Materials to Avoid)	Avoid direct contact with strong acid.
HAZARDOUS DECOMPOSITION PRODUCTS	NO_x
HAZARDOUS POLYMERIZATION ☐ May Occur ☒ Will Not Occur	CONDITIONS TO AVOID

(over)

1

FINISH MATERIAL

ARVIN/CALSPAN
ADVANCED TECHNOLOGY CENTER

April 16, 1984
JGM:jas 788-012

Mr. Henry C. Duwe
Plant Engineer
Moench Tanning Company
Gowanda, NY 14070

Dear Mr. Duwe:

On 27 March 1984, Mr. Jack Fisher and Mr. Eugene Rabent sampled the wells at your Point Peter Road Landfill. Wells were bailed previously by your personnel and allowed to recharge prior to sampling. Sampling was conducted by use of a hand bailer located in each well casing.

Results of analysis of the collected samples are attached. Also attached is the height of water in the wells from the top of the PVC casing. I have also included the results obtained from your sludge samples analyzed for chromium and lead. Results include a "total" analysis and an EPA standard leach test.

If you have any questions on the results or the method of analysis, please contact me at 631-6771.

Sincerely,

John G. Michalovic

John G. Michalovic
Head, Chemical Analysis Section
Environmental Sciences Department

Enclosures

ATG
ARVIN
ARVIN/CALSPAN ADVANCED TECHNOLOGY CENTER P.O. BOX 400, BUFFALO N.Y. 14225 TEL (716) 632-7500
APPLIED TECHNOLOGY GROUP OF ARVIN INDUSTRIES INC Cable CALSPAN / Telex 91-270

MOENCH TANNING

Sludge Sampling

Received 2/27/84

SAMPLE	Pb(EP)* mg/l	Pb(total) µg/g	Cr(EP)* mg/l	Cr(total) µg/g
#1 New Finish Dept. Spray Booth Sludge	0.393	9,060	0.017	3,340
#2 Old Finish Dept. Spray Booth Sludge	<0.010	3.0	<0.010	2.0
#3 New Finish Dept. Band Cleaning	10.6	18,140	0.822	4,158
#4 Old Finish Dept. Band Cleaning	0.173	239	0.455	90

*EP - Extraction Procedure - EPA Standard Leach Test

ecology and environment, inc.
International Specialists in the Environmental Sciences

LABORATORY REPORT

FOR

Moench Tanning

Job No.: MT-U-0025

Sampled By: Client

Date Received: 3/2/84

Delivered By: Client

E & E Lab Number	752	753	754	755
Customer Number				
Sample Identity	#1 Old Band Cleaning	#2 Old Booth Sludge	#3 New Booth Sludge	#4 New Band Cleaning
Flash Point, °F	Non Flammable(1)	Non Flammable(1)	Non Flammable(1)	Non Flammable(1)

(1) Samples are ignitable but do not flash.

Analytical References:

"Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, "SW-846, Second Edition, U.S. EPA, 1982.

Supervising Analyst Gary Hahn

Date: 4-25-84

March 8, 1979

Mr. Hank Duwe
Moench Tanning Co., Inc.
265 Palmer Street
Gowanda, New York 14070

Re: Leaching Potential Test Results (RENDERING WASTE)

Dear Mr. Duwe:

Please find enclosed Recra Research, Inc.'s results of the analyses of the sludge sample received at our laboratories on 1/29/79 referenced above.

Analyses of Total Chlorinated Hydrocarbons (TCH) could not be completed due to solidification of the concentrated extracts. Numerous attempts were made to correct this situation. The solidified materials were thought to be sulfate salts, however, water washing the extract failed to remove the solids present. It is also possible that these solid materials in the extract are fats, greases or lipid type substances which were co-extracted in the standard TCH procedure.

If you have any questions concerning these data, do not hesitate to contact the undersigned.

Sincerely,

RECRA RESEARCH, INC.

Robert K. Wyeth
Laboratory Director

RKW:df
Enclosure
cc: R. A. Stadelmaier
K. C. Malinowski

RECRA RESEARCH, INC. 111 Wales Avenue/Tonawanda, New York 14150/(716) 692-7620
TOTAL CHEMICAL WASTE MANAGEMENT THROUGH APPLIED RESEARCH

ANALYTICAL RESULTS
MOENCH TANNING
NEW YORK STATE LEACHING POTENTIAL TEST

Report Date: 3/7/79
Date Received: 1/29/79

PARAMETER	UNITS OF MEASURE	SAMPLE IDENTIFICATION SLUDGE
Dry Weight (103°C)	%	26.3
Acidity (pH 8.3)	mg/g (dry) as $CaCO_3$	36.2
Chemical Oxygen Demand	mg/g (dry)	735
Total Grease & Oil	mg/g (dry)	342
Hydrocarbon Grease & Oil	mg/g (dry)	10
Polar Grease & Oil	mg/g (dry)	332
Total Cadmium	µg/g (dry)	<0.53
Total Copper	µg/g (dry)	14.8
Total Chromium	µg/g (dry)	22.4
Total Iron	µg/g (dry)	464
Total Manganese	µg/g (dry)	<3
Total Lead	µg/g (dry)	16
Total Zinc	µg/g (dry)	18.1
Total Arsenic	µg/g (dry)	0.49
Total Mercury	µg/g (dry)	<0.06
Total Selenium	µg/g (dry)	<0.80
Total Chlorinated Hydrocarbons	µg/g (dry) as Chlorine; Lindane Standard	-

COMMENTS: Comments presented pertain to data on one or both of the pages of this data report. All analyses were performed according to methods presented in the U.S. Environmental Protection Agency manual of Methods for Chemical Analysis of Water and Wastes, or the 14th Edition of Standard Methods for the Examination of Water and Wastewater.

FOR RECRA RESEARCH, INC. ____________________

DATE 3/8/79

ANALYTICAL RESULTS
MOENCH TANNING
NEW YORK STATE LEACHING POTENTIAL TEST

Report Date: 3/7/79
Date Received: 1/29/79

PARAMETER	UNITS OF MEASURE	SAMPLE IDENTIFICATION	
		DECANTATE	LEACHATE
Acidity (pH 8.3)	mg/l as $CaCO_3$	-	1,660
Chemical Oxygen Demand	mg/l	36,700	5,970
pH	Standard Units	1.44	2.20
Total Dissolved Solids (103°C)	mg/l	52,800	-
Ammonia	mg N/l	-	54.2
Sulfate	mg/l	-	1,700
Total Organic Carbon	mg/l	16,500	2,140
Soluble Cadmium	mg/l	0.006	0.008
Soluble Copper	mg/l	1.32	0.116
Soluble Chromium	mg/l	1.90	0.050
Soluble Iron	mg/l	3.8	1.0
Soluble Manganese	mg/l	1.6	0.19
Soluble Lead	mg/l	0.16	0.04
Soluble Zinc	mg/l	6.62	0.890
Soluble Arsenic	µg/l	4.2	2.3
Soluble Mercury	µg/l	0.9	<0.6
Soluble Selenium	µg/l	<3	<3
Total Chlorinated Hydrocarbons	µg/l as Chlorine; Lindane Standard	-	-

COMMENTS: Total Chlorinated Hydrocarbon analyses could not be completed due to solidification of the concentrated extracts. Attempts to remove the solid materials, through to sulfate salts, by washing the extracts with water was unsuccessful. Values reported as "less than" indicate working detection limits for the particular sample/parameter.

FOR RECRA RESEARCH, INC.

DATE 3/8/79

FINISH MATERIAL 1

RECRA RESEARCH, INC.
Hazardous Waste And Toxic Substance Control

November 17, 1983

Mr. Henry C. Duwe
Moench Tanning Co.
Beech and Palmer Streets, Box 389
Gowanda, New York 14070

Dear Mr. Duwe:

Please find enclosed the report regarding the waste characterization performed on the sample labelled Spray Booth Sludge and Band Cleaning, received at Recra Research, Inc. on August 23, 1983.

If you have any questions or if I can be of further assistance to you, please do not hesitate to contact me. We look forward to being of continued service to you in the future.

Sincerely,

RECRA RESEARCH, INC.

Brian C. Senefelder

Brian C. Senefelder
Laboratory Supervisor
Waste Materials Management

I.D. #3W-120

BCS/af
Enclosure

HAZARDOUS WASTE ASSESSMENT
performed for
MOENCH TANNING COMPANY

Report Date: November 17, 1983

SAMPLE IDENTIFICATION: Spray Booth Sludge, Band Cleaning

IGNITABILITY

The waste samples were evaluated for the characteristic of ignitability on the basis of the flash point determinations only.

Section 261.21(a)(1) of the Title 40 CFR states that a solid waste exhibits the characteristic of ignitability if a representative sample of the waste is a liquid, other than an aqueous solution, containing less than 24 percent alcohol by volume, and has a flash point less than 60°C (140°F), as determined by a Pensky-Martens Closed Cup Tester, using the test method specified in ASTM Standard D-93-79.

Utilizing the Test Method 1010 specified in Test Methods for Evaluating Solid Waste; Physical/Chemical Methods, SW 846, July, 1982, 2nd edition, the flash point of the waste samples were determined to be the following:

	RUN I	RUN II
Spray Booth Sludge	109°F	105°F
Band Cleaning	123°F	124°F

Based on the flash point determinations the waste samples do appear to exhibit the characteristic of ignitability and should be assigned a Hazardous Waste Number of D001 and Hazard Code "I".

FOR RECRA RESEARCH, INC. Brian C. Snefelder

DATE 11/17/83

I.D. #3W-120

HAZARDOUS WASTE CHARACTERIZATION
performed for
MOENCH TANNING COMPANY

PARAMETER	UNITS OF MEASURE	SPRAY BOOTH SLUDGE	
Form	-	Wet Solid Sludge	
Color	-	Pink/Purple	
Turbidity	-	Opaque	
Viscosity	-	High	
Odor	-	Pungent/Sweet Odor	
Layering	-	Free Liquid	
Density	@ 25°C g/cm^3	1.10	
pH	Standard Units	4.19 (with H_2O)	
Flash Point (Pensky Martens Closed cup)	°F	Run I 109	Run II 105
Heat of Combustion	BTU/lb	2,600	
Ash weight @ 550°C	% by weight	18.0	

COMMENTS: Above analyses performed in accordance with EPA/ASTM methodologies where applicable.

FOR RECRA RESEARCH, INC. Brian C. Senefelder

DATE 11/19/83

I.D. #3W-120

HAZARDOUS WASTE CHARACTERIZATION
performed for
MOENCH TANNING COMPANY

PARAMETER	UNITS OF MEASURE	BAND CLEANING
Form	-	Solid
Color	-	White
Turbidity	-	Opaque
Viscosity	-	High
Odor	-	Pungent Odor
Layering	-	-
Density	g/cm^3	0.8
pH	Standard Units	7.12 (with H_2O)
Flash Point (Pensky Martens Closed cup)	°F	Run I Run II 123 124
Heat of Combustion	BTU/lb	7,400
Ash weight @ 550°C	% by weight	25.0

COMMENTS: Above analyses performed in accordance with EPA/ASTM methodologies where applicable.

FOR RECRA RESEARCH, INC. ______

DATE 11/19/83

I.D. #3W-120

RECRA RESEARCH INC.

GAS CHROMATOGRAPHIC ANALYSIS
performed for
MOENCH TANNING COMPANY

Report Date: November 17, 1983

SAMPLE IDENTIFICATION: Spray Booth Sludge (Liquid phase)

Constituent	Composition (% by weight)
Water	58
Ethanol	<1
Pentane	<1
Carbon Tetrachloride	<1
Heptane	<1

Comments

Gas chromatographic analysis was performed by direct injection of the sample into a GOW-MAC Series 550P G.C. equipped with a Poropack Q column and thermal conductivity detection. The total run time was 25 minutes with a maximum temperature of 240°C. The scan procedure employed is designed to examine for common solvents such as low molecular weight alcohols, normal hydrocarbons, aromatic hydrocarbons, ketones, ethers and esters as well as common chlorinated and fluorinated solvents.

Identification of specific constituents was based upon comparison of retention times of peaks which appeared in the chromatogram of the sample with those of standard compounds.

The total % identified was 60%.

The remaining 40% could not be identified under the specified conditions; further analysis would be required.

The percent by weight of each constituent was calculated based upon a density of 1.10 g/ml measured on the original sample.

RECRA RESEARCH, INC. Brian C. Senefelder

DATE 11/17/83

RECRA RESEARCH, INC.

I.D. #3W-120

HAZARDOUS WASTE ASSESSMENT
performed for
MOENCH TANNING COMPANY

Report Date: November 17, 1983

SAMPLE IDENTIFICATION: Spray Booth Sludge, Band Cleaning

EP TOXICITY

The waste samples subjected to the EP Toxicity Test procedure as defined in Test Method 1310 specified in Test Methods for Evaluating Solid Waste; Physical/Chemical Methods, SW 846, July 1982, 2nd edition.

The waste samples contained greater than 0.5 percent filterable solids; therefore, they were extracted according to protocol.

The resultant extracts were analyzed for the metal contaminants only as listed in Test Method 1310. The results of these analyses are listed in this report.

The analyzed lead concentration of the EP Toxicity Test Extract for the "Spray Booth Sludge" sample does exceed the maximum allowable concentration listed in the October 30, 1980 amended Title 40 CFR. Therefore, the sample labelled "Spray Booth Sludge" exhibits the characteristic of EP Toxicity and should be assigned an EPA Hazard Code of "E" and an EPA Hazardous Waste Number of "D008", designating lead contamination. The sample labelled "Band Cleaning" does not appear to exhibit the characteristic of EP Toxicity (for metals only).

RECRA RESEARCH, INC. Brian C.

DATE 11/17/83

I.D. #3W-120

RECRA RESEARCH, INC

ANALYTICAL RESULTS

MOENCH TANNING
EP TOXICITY TEST EXTRACTS

Report Date: 11/14/83

PARAMETER	UNITS OF MEASURE	SAMPLE IDENTIFICATION		EPA MAXIMUM CONCENTRATION (mg/1)
		SAMPLE #1 SPRAY BOOTH SLUDGE	SAMPLE #2 BAND CLEANING	
Total Arsenic	mg/1	<0.005	<0.005	5.0
Total Barium	mg/1	0.63	0.71	100.0
Total Cadmium	mg/1	0.005	0.005	1.0
Total Chromium	mg/1	2.00	0.330	5.0
Hexavalent Chromium	mg/1	0.968	0.056	-
Total Lead	mg/1	10.9	0.827	5.0
Total Mercury	mg/1	<0.001	<0.001	0.2
Total Silver	mg/1	<0.008	<0.008	1.0
Total Selenium	mg/1	<0.005	<0.005	5.0

COMMENTS:

Methods used for the EP Toxicity Test procedure as well as the analysis of the resulting extracts were presented in U.S. Environmental Protection Agency publication, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods; SW-846, Second Edition, 1982. Metals analyses were performed utilizing the method of standard addition. Values reported as "less than" (<) indicate the working detection limit for the particular sample or parameter.

FOR RECRA ENVIRONMENTAL LABORATORIES

DATE 11/14/83

RECRA ENVIRONMENTAL LABORATORIES

I.D. #83-885/3W-120

ANALYTICAL RESULTS

MOENCH TANNING

Report Date: 11/14/83

PARAMETER	UNITS OF MEASURE	SAMPLE IDENTIFICATION TOTAL METALS SAMPLE #1	TOTAL METALS SAMPLE #2
Total Lead	µg/g	56.8	10,500
Total Iron	µg/g	3,530	3,240
Total Titanium	µg/g	255	73
Total Molybdenum	µg/g	104	232
Total Chromium	µg/g	717	2,730
Hexavalent Chromium	µg/g	5.95	12.2

COMMENTS:

Analyses were performed according to U.S. Environmental Protection Agency methodologies.

FOR RECRA ENVIRONMENTAL LABORATORIES

DATE 11/14/83

RECRA ENVIRONMENTAL LABORATORIES

I.D. #83-885/3W-120

18. Chemistry of the Vegetable Tannins

Theodore White

Forestal Central Laboratories, Harpenden, England

The vegetable-tannin extracts form a heterogeneous group of materials having in common a capacity to convert animal skins into leather. The term "tannin" was introduced by Seguin[218] to denote the substances responsible for the leathering ability of various plant extracts; unless a substance can be shown to possess this function, it cannot be termed a tannin. The chemical and botanical literature contains many examples of tannins identified as such by chemical tests which are indicative of phenols but not necessarily of a capacity to make leather. This has complicated the literature to an extent which makes a definitive survey of the present position of tannin chemistry difficult.

In the main, this survey of vegetable-tannin chemistry will deal, therefore, with those plant extracts which are used for the industrial production of leather, with such addition as is required to give a balanced but critical view of progress in the field as a whole. The writer and his colleagues have emphasized that tannin extracts are complex mixtures of many substances, and that it is rarely possible to single out any one substance from an extract and regard it as the characteristic tannin of the plant concerned. The recognition of this complexity has made it more difficult than ever to define a tannin, and, at present, it is generally safer to use the term "tannin extract," acknowledging that many substances are present in an extract and that they may vary in formula type as well as in detail.

Vegetable-tannin extracts tan because they contain polyphenolic substances. The simpler, smaller-molecular-weight phenols and those containing only low proportions of phenolic groups do not tan, and a minimum molecular weight appears to be essential. This minimum probably varies with the nature of the molecule and the number of phenolic groups present, and at its lowest cannot be much below 400 to 500. Work on synthetic tannins suggests that molecular weights above 3,000 lead to a deficient tanning action because of poor penetration into the collagen fibrils, and recent work indicates that most natural tannins have molecular weights within these limits. This rules out from the true tannins substances such as catechin, chlorogenic acid, the anthocyanidins, and other simple phenolic

substances often identified as tannins by purely chemical tests. Many of these simple substances precipitate gelatin, as shown by Jones,[101] or are partially retained by hide powder under the normal conditions of tannin analysis, so that even these tests are not specific for tannins. The structural stability conferred on hide by tannage with vegetable extracts is undoubtedly due to crosslinking of collagen molecules by multivalent tannin molecules, and a certain minimum size of the crosslinking agent and minimum number of crosslinking phenolic groups must be necessary. It is possible that any carbon skeleton which allows these requirements to be provided might be satisfactory and, in that event, a general similarity of carbon skeleton throughout the range of different tannin extracts need not be postulated.

Plants produce many different types of phenolic molecules, and many more of these types may participate in the structures of the substances in tannin extracts than has been accepted hitherto. Although the simpler phenolic molecules do not tan, some of them undoubtedly contribute to the creation of optimum conditions of tannage, while others (e.g., ellagic acid "bloom") undoubtedly affect the physical characteristics of leathers in which they are physically deposited in insoluble form, rather than chemically combined. In such cases it is impossible to demarcate tannins clearly from nontannins, particularly since it is known that mutual solubilization can cause substances, which themselves have no true tanning action, to function apparently as tannins under practical conditions.

The minimum size and reactivity necessary for tanning capacity can be achieved in various ways. The most common in nature seems to be by ester linkage of gallic acid or related substances to a central carbohydrate core. Tannin molecules built up in this way are readily broken down by hydrolysis with acids, alkalies, or enzymes and are termed "hydrolyzable tannins." They commonly possess free acidic carboxyl groups in addition to phenolic groups.

In contrast, certain other water-extractable polyphenol mixtures present in plants contain only small amounts of carbohydrates, and these are not chemically linked to the phenolic substances present. They contain only traces of gallic acid and similar substances, and fail to give significant yields of simple easily crystallizable phenolic molecules on hydrolysis. These extracts are generally termed the "condensed tannins" or "nonhydrolyzable tannins." Neither term is really satisfactory. The most serious objection to grouping these extracts under one name is that it has been taken to imply structural similarity throughout the group, and it is doubtful if such uniformity exists. For the present, however, the term "condensed tannins" can be retained, provided it is understood that not all the tannin extracts grouped under this heading are necessarily alike. Their diversity of origin from widely differing plant species and the complexity of their composition should, in any case, leave this no longer in doubt.

Geissman and Hinreiner[66] provided a list of naturally occurring phenolic substances which they considered relevant to a discussion of flavanoid biogenesis, and it can be equally well applied to tannin chemistry. More than two dozen types were involved and, with so many different reactive phenolic nuclei spread throughout the plant kingdom often occurring as minor components of tannin extracts, and so little known about the structure of condensed tannins, the problem of surveying tannin chemistry can be approached only with caution. The chemistry of the hydrolyzable tannins can be dealt with on the basis of the combination of sugars with gallic acid, or substances related to it. In the condensed tannins, catechin plays an important role in some extracts, leucoanthocyanidins in others, but in the rest all that can safely be said is that the presence of di- and trihydric phenol nuclei can be readily demonstrated (e.g., catechol, pyrogallol, resorcinol, phloroglucinol). The manner in which these nuclei are linked to form tannin molecules is not yet known, and it would be unwise at this stage to rule out the possibility of structures other than those suggested to date.

This is a more complex view of tannin chemistry than is general at present. The simpler orthodox position is stated in earlier reviews and books where the historical development of the field is adequately surveyed and where it has been customary to deal with the subject "tannin" by "tannin." A complete list of earlier surveys is unnecessary, but the following constitute essential reading: Gnamm,[68] Rottsieper,[181] Thorpe,[231] Dekker,[44] Howes,[97] Stather,[225] Pawlowitsch,[158] Perkin and Everest,[159] Nierenstein,[150] Freudenberg,[57, 58] Fischer,[54] Procter and Paessler,[168] Wilson,[259] McLaughlin and Theis,[136] and B.L.M.R.A.[20]

HYDROLYZABLE TANNIN EXTRACTS

The members of this group which are of greatest importance in view of the extent of their use and their scientific interest are:

Tannic acid—*Aphis chinensis* galls on leaves of *Rhus semialata* (Anacardiaceae)
Turkish tannin—*Cynips tinctoria* galls on twigs of *Quercus infectoria* (Fagaceae)
Sumach extract—leaves of *Rhus coriaria* (Anacardiaceae)
Tara extract—pods of *Caesalpinia spinosa* (Leguminosae)
Valonia extract—acorn cups of *Quercus Aegilops* (Fagaceae)
Myrobalan extract—fruit of *Terminalia chebula* (Combretaceae)
Divi-divi extract—pods of *Caesalpinia coriaria* (Leguminosae)
Algarobilla extract—pods of *Caesalpinia brevofolia* (Leguminosae)
Oak extract—bark and wood of various *Quercus* spp. (Fagaceae)
Chestnut extract—bark and wood of *Castanea sativa* and *dentata* (Fagaceae)

With the exception of tannic acid, little was known of the chemistry of these extracts until recent years except that they were largely gallic acid derivatives of sugars. The writer and his colleagues included most of them in the earliest paper chromatography studies of the tannins (White;[252] Kirby, Knowles, and White;[115] White, Kirby, and Knowles[256]) and showed that each extract consisted of a number of different substances. The nature of some of these is now known as a result of the work of Schmidt and his colleagues,[203-207, 209-217] and, except in the case of tannic acid, it is rare for a single component to dominate the extracts. The complexity of composition should be kept constantly in mind in reading the following survey.

The Gallotannins or Tannic Acids. The chemistry of these extracts commenced with the observations of Macquer and Monnet,[137] Scheele,[200] Kunsemüller,[124] Berthollet,[18] and others who isolated from plant galls the material termed by Scheele "gallapfelsaure," by Proust[164] "tannin," and by other workers "gallotannin" and "tannic acid." Little progress was made in determining its chemical nature until the early 1900's by which time it was accepted that acid or enzyme degradation yielded only gallic acid and glucose. The investigations ultimately focused on tannic acid from Chinese galls and Turkish tannin from Turkish galls, and the uncertainty of the results can be seen in the quotation of molecular weights ranging from 340 to 3,700 for the purified tannin from each of these sources.

The classical work of Fischer[54] and his collaborators over the period from 1908 to 1918 led to the formulation of tannic acid as penta-*m*-digalloylglucose and Turkish tannin as pentagalloylglucose, with ellagic acid playing an uncertain role in this second extract. Fischer synthesized pentagalloyl and penta-*m*-digalloylglucose and found them amorphous, like his natural products. He found similarities between the synthetic and natural materials, but also observed solubility differences which introduced a degree of uncertainty into the comparison. He undoubtedly regarded all the glucose hydroxyl groups as esterified in both tannins.

Karrer, Salomon, and Peyer[105] and Karrer[104] fractionated tannic acid and Turkish tannin by precipitation with aluminum hydroxide and concluded that tannic acid was basically a pentagalloylglucose molecule of the type envisaged by Fischer, with varying proportions of the galloyl hydroxy groups further esterified with gallic acid. The glucose molecule was envisaged as fully substituted and as carrying a small proportion of galloyl groups, a larger proportion of *m*-digalloyl groups, and possibly a few higher linear ester groupings (e.g., trigalloyl forms). A number of such substances were believed to be present, differing only in detail, with octa- and nonapyruvate → glucose → sedoheptulose diphosphate → shikimic acid, a combination of the two sequences could constitute a path from initial photosynthesis to the aromatic nuclei of the essential amino acids in plants. Brown and Neish[29] suggested that this might be the source of aromatic nuclei generally in plants and, by feeding radioactive shikimic acid to plants, showed that this produced radioactive lignin, suggesting that shikimic acid is a precursor of the aromatic ring of lignin. In consequence, Burton and Nursten[33] and also Hathway[81] postulated that shikimic acid might be a precursor of the tannins in plants, the former authors pointing out that since Catravas[36] had found shikimic acid in sumach extract, the origin of hydrolyzable tannins might lie in a switch of aromatic biosynthesis at the shikimic acid step, leading directly or indirectly to gallic acid and its derivatives. This was strongly supported by Hathway's[81] demonstration that quinic acid and shikimic acid are the principal acids in myrobalan fruits, with lesser amounts of dihydro- and 5-dehydro shikimic acids also present. Since then, Eberhardt and Schubert[48] have shown that if shikimic acid, having C atoms 2 and 6 of the ring radioactive, is supplied to sugar-cane leaves, the lignin subsequently isolated from the stem of these plants can be oxidized to vanillin in which the corresponding C atoms 2 and 6 of the ring are similarly and comparably radioactive.

This evidence that shikimic acid can be a precursor of the aromatic ring of lignin, and its obvious close relationship to gallic acid, makes it seem probable that the galloyl and related groups of the hydrolyzable tannins may also arise, at least in part, by the metabolic path suggested above, although other metabolic paths may also be operating. Application of the Eberhardt and Schubert technique to the leaves of *Rhus* sp., followed by isolation and hydrolysis of the gallotannin from the leaves, should soon provide evidence whether or not this is correct. The evidence from the work of King and White[113b, c] (discussed later) that in the case of Quebracho there is a biogenetic link between condensed and hydrolyzable tans, with quinic acid derivatives also involved is of importance here.

The final point that should be made is that the hydrolyzable tannin extract components so far identified are but a dozen in number, and most of them constitute only a small part of the extracts. Chromatograms show that many more substances remain for identification; in the light of this and the new work on shikimic acid, this field of study seems likely to continue to yield results of interest for some time to come. As an aid to investigation Figure 2 is given as a reference two-way chromatogram of chebulinic acid, chebulagic acid, corilagin, glucogallin, 3,6-digalloylglucose, hexahydroxydiphenic acid (kindly supplied by Professor Schmidt), ellagic acid, *m*-digallic acid, and gallic acid.

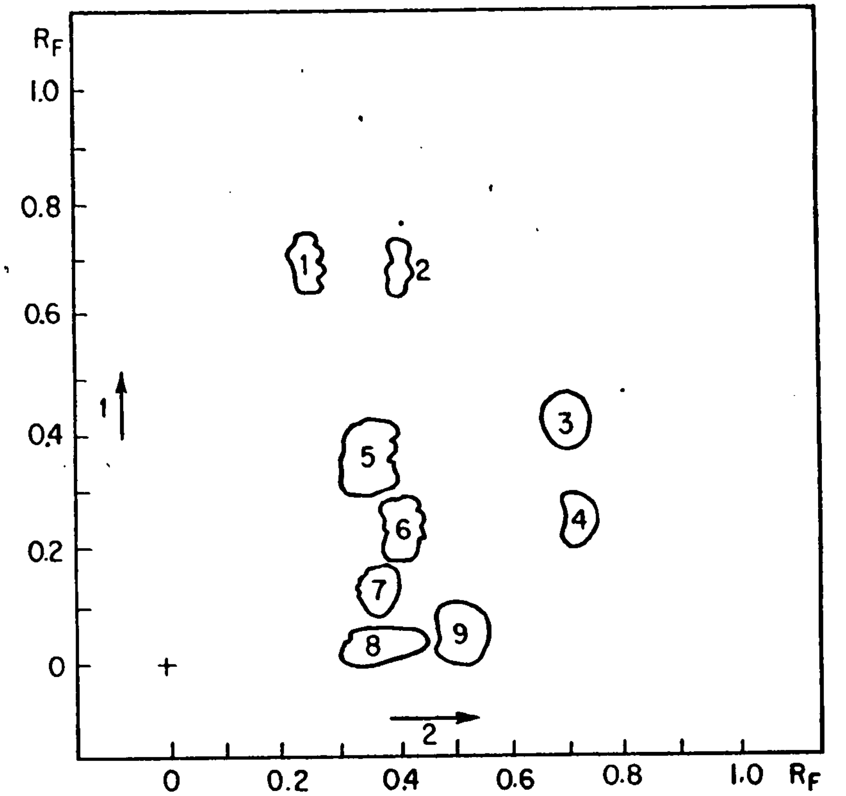


FIG. 18·2. *Two way chromatogram of key substances from hydrolysable extracts.* Chromatographed with 6 per cent acetic acid (first way) followed by sec-butanol/acetic acid/water, 14:1:5 (second way). Components: 1. Hexahydroxydiphenic acid 2. β-glucogallin, 3. Gallic acid, 4. *m*-Digallic acid, 5. Corilagin, 6. 3,6-Digalloylglucose, 7. Chebulagic acid, 8. Ellagic acid, 9. Chebulinic acid.

CONDENSED TANNIN EXTRACTS

The most important tannin extracts of this group are contained in the following list.

Gambier extract—leaves and twigs of *Uncaria gambier* (Rubiaceae)
Catechu (Burma cutch) extract—wood of *Acacia catechu* (Leguminosae)
Quebracho extract—wood of *Schinopsis lorentzii, balansae* (Anacardiaceae)
Wattle extract—bark of *Acacia mollissima* (Leguminosae)
Tizerah extract—wood and roots of *Rhus pentaphylla* (Anacardiaceae)
Urunday extract—wood of *Astronium balansae* (Anacardiaceae)
Mangrove extract (Borneo cutch)—bark various *Rhizophoraceae spp.*

Hemlock extract—bark of *Tsuga canadensis* (Pinaceae)
Spruce extract—bark of *Picea abies* (Pinaceae)
Larch extract—bark of *Larix decidua* (Pinaceae)
Tea tannins—leaves of *Camellia sinensis* (Theaceae)

Except for the first four extracts and the tea tannins, little is known of the chemistry of these materials. The eucalyptus kinos and extracts probably also belong in this group, but the products available are made from wood and bark combined and contain both condensed and hydrolyzable tannins as a result of this admixture.

Hypotheses of Tannin Structure. There has undoubtedly been much hypothesis in the work published to date on the chemistry of the condensed tannin extracts. Many of the papers and surveys, while admitting the extracts to be mixtures, have concentrated on providing a single structural formula for each extract—the two concepts being incompatible. The main lines of approach to date are as follows: (1) the catechin hypothesis of condensed tannin structure put forward by Freudenberg[57] claiming that the condensed tannins are polymers of catechins; (2) the flavpinacol hypothesis of Russell,[190, 191, 196] a dimeric structural variant of the catechin hypothesis; (3) the leucoanthocyanidin hypothesis, a recent development whereby the finding that many chemically identified tannins of the botanical literature are really leucoanthocyanidins is claimed to provide a new interpretation of condensed tannin chemistry; and (4) the Forestal observations of the writer and his colleagues[115, 116, 117, 118, 119, 120, 248, 250, 251, 252, 256] that tannin extracts are complex in composition and that each contains an appreciable number of polyphenolic substances—many of which are tannins in their own right. The behaviour of an extract is very dependent on this complexity; each individual polyphenol in an extract (and probably certain nonphenolic substances) may play a part in tannage, and there can be no question of a single structural formula for any extract.

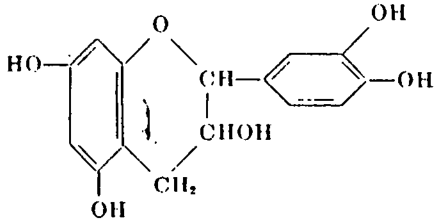
This latter view is felt to put the structural hypotheses into proper perspective, and the development of the subject as a whole can be seen by dealing first with catechin, then with the tea catechins, the leucoanthocyanidins, and finally with the chemistry of quebracho and wattle extracts considered jointly. Any attempt to consider the remaining condensed tannin extracts in detail would confuse the account without adding to our understanding, in view of the little that is known of their chemistry.

The Catechin Hypothesis. Until recently, studies of the chemistry of the condensed tannin extracts revolved around the catechin hypothesis stated by Freudenberg.[57] Perkin and Everest[159] had already recorded suggestions as to a relationship between catechin and the condensed tannins, but Freudenberg adopted the term "catechins" as a collective name for those substances in plant extracts which resembled catechin in yielding phloroglucinol (later resorcinol) and protocatechuic acid on alkali fusion, and in giving amorphous insoluble products—phlobaphenes or reds on heating with mineral acids. His basic thesis was that most flavonoid substances are based on phloroglucinol linked to catechol by a ring system involving a 3-carbon chain, and since a similar skeleton characterized the anthocyanidins and catechins, it must also be present in the condensed tannins. These, since their reactivity resembled that of catechin, must be polymers of catechin, not of the related flavonoids or anthocyanins also present in the extracts.

The hypothesis was recently restated by Freudenberg and Weinges[64] in these words: "Natural tannins are polymerizates, condensates or dehydration-polymerizates of reactive catechins. . . . Plants build up from catechins the soluble, sparingly soluble and insoluble tannins and tannin-reds (phlobaphenes) in two ways. The one process is post-mortal and consists of the above mentioned polycondensation under the influence of moisture and acidity often over a prolonged period. The other process is accomplished under the influence of dehydrases and proceeds by spontaneous elimination of hydrogen from the phenol groups without direct assistance from enzymes. This second process is analagous to the formation of lignin from *p*-hydroxy cinnamyl alcohol."

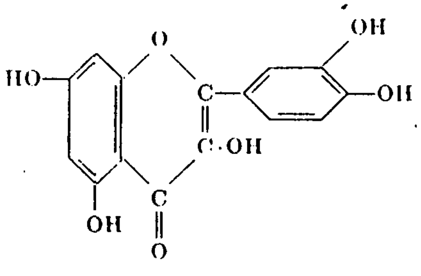
The evidence for the importance of catechin in condensed tannin extracts is confined largely to gambier and Burma cutch extracts (although Mayer[143] has recently demonstrated the existence of catechin and gallocatechin in oak and chestnut barks) and has not really been shown to apply to other materials used for tanning. The concept would seem, in the light of our present knowledge, to be unduly rigid and, by suggesting a relationship which may not exist between tannin extracts from widely separated species and from vastly differing tissues, it probably gives too simple a view of the processes underlying their origin.

The catechin hypothesis arose initially because of earlier observations that certain phenols and phenol carboxylic acids arose from alkali decomposition of condensed tannin extracts. The only substance which could readily be isolated in crystalline form from any of these extracts was catechin, and it was observed in significant amounts only in gambier and Burma cutch. Freudenberg found the substance to be highly reactive and readily converted to an amorphous product capable of tanning hide, and he set out to determine its structure. The way in which he achieved this is summarized by Mason[140] and by Freudenberg.[58] He ultimately found that catechin existed in six isomeric forms—D-catechin, L-catechin, *r*-catechin, D-epicatechin, L-epicatechin and *r*-epicatechin—and showed how the various interconversions of these products could take place on the basis of the formula

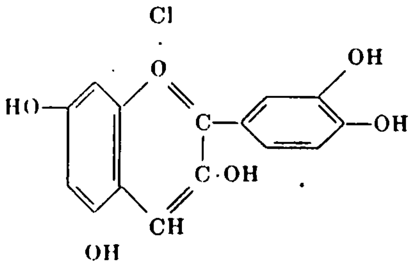


catechin

In accordance with this formula, catechin yielded phloroglucinol and protocatechuic acid on alkali fusion, as do many of the condensed tannin extracts. It is found in association with other substances such as flavonols and anthocyanidins, which possess similar carbon skeletons built up of a phloroglucinol nucleus linked to a catechol nucleus via a six-membered pyran ring, e.g., quercetin and cyanidin.



quercetin



cyanidin chloride

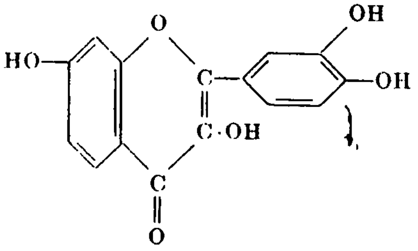
The reduction of pentamethyl cyanidin to pentamethyl DL-epicatechin by Freudenberg, Fikentscher, Harder, and Schmidt[59] and of pentamethyl quercetin to pentamethyl DL-epicatechin by Freudenberg and Kammüller,[60] and oxidation of tetramethyl-D-catechin to cyanidin chloride by Appel and Robinson[3] were, in fact, determinant experiments in settling the previously controversial structure of catechin.

In the case of gambier and Burma cutch extracts, it can be seen in the two-way paper chromatograms published by White, Kirby, and Knowles[256] that catechin is an important constituent of these extracts, and in gambier extract it forms about 50 per cent of the water-soluble content. In both extracts, however, other polyphenolic substances of unknown structure are also present and, in view of the emphasis laid by Freudenberg[57, 58] on the fact that both catechin and the condensed tannin extracts generally produce reds on treatment with mineral acid, it is as well to point out that in fact catechin does *not* produce a red precipitate with mineral acids; the insoluble matter produced is a light cream color, as was shown by Bate-Smith.[8] The most recent work in this field by Hathway,[81a] and Hathway & Seakins,[81b,c,d] has clarified the position somewhat in showing that catechin can undergo polymerization during autoxidation at neutral pH and that the process involves quinone polymerization. A similar polymer was obtained by polyphenoloxidase treatment and both polymers were found to be strikingly similar in properties to "phlobatannins" isolated from both Gambier and Burma Cutch extractives, suggesting that head-to-tail quinone polymerization of catechin is the most likely mechanistic basis of its participation in the formation of tannin extracts of the Cutch and Gambier types. Further evidence for this came from the fact that oxidative degradation of the methylated-hydrogenated-catechin-autoxidation polymer produced, among other substances, small amounts of metahemipinic acid.

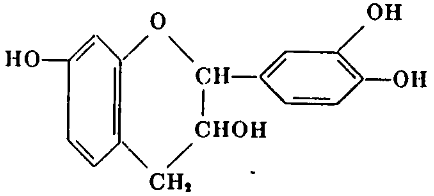
The presence of such large amounts of catechin in gambier and Burma cutch suggests that these two extracts should be regarded as constituting a subgroup of their own. The phlobaphene test for condensed tannins, i.e., the formation of an insoluble red precipitate on boiling an extract with mineral acid, can, in fact, be used to distinguish different subgroups of the condensed tannins, if gambier and Burma cutch are accepted as a subgroup by virtue of their high catechin content. The eucalyptus and mangrove extracts can be linked as a second subgroup (see later), since the red color of their phlobaphenes can be shown chromatographically (Hillis,[92] King and White[113]) to be due to the fact that as much as 10 per cent of anthocyanidins is formed when these extracts are heated with mineral acid. The remaining condensed tannins neither contain large amounts of catechins nor give high yields of anthocyanidins in this phlobaphene test *as applied by these authors.*

In view of the amounts of recognizable substances involved in the case of the first two subgroups, these are major differences, far more so than any previously observed, and they show clearly that from the structural viewpoint the condensed extracts do not constitute a homogeneous group.

The application of the catechin concept to Burma cutch and gambier seems reasonable, but the suggestion of Freudenberg, Fikentscher, Harder, and Schmidt[59] and of Freudenberg and Maitland[62, 63] that the chemistry of quebracho extract could be explained on this basis must be treated as hypothesis. After earlier workers showed the formation of resorcinol and protocatechuic acid on fusing quebracho extract with alkali, Freudenberg and Maitland based this hypothesis on the occurrence in the extract of the yellow-fluorescing flavonol fisetin which differed from the quercetin of Burma cutch in containing a resorcinol group in place of the latter's phloroglucinol.



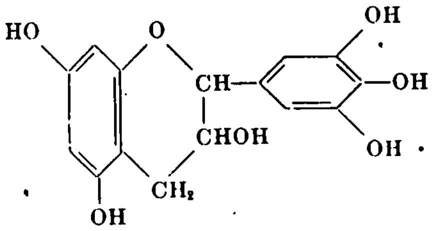
fisetin



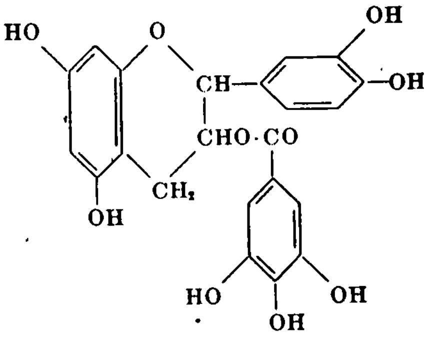
hypothetical quebracho catechin

To the idea that quebracho tannin existed as an individual entity and that it was a polymer of a catechin, they added the idea that the catechin from which it was formed had a disposition of its phenolic groups similar to that of fisetin. They then synthesized this quebracho catechin and showed its conversion by acids or on boiling in water to an amorphous, presumably polymeric, polyphenol which could tan hide. Russell's attempt[190, 191] to put forward his flavpinacol hypothesis of condensed tannin structure on a similar basis was severely criticized by Freudenberg and Steinbrunn,[61] although Freudenberg and Maitland[62, 63] presented a formula illustrating the way in which quebracho tannin was built up from their hypothetical quebracho catechin without any trace of the latter having been found in the extracts. The latest statement of the catechin hypothesis by Freudenberg and Weinges[64] is again based on the conversion of various synthetic catechins into amorphous insoluble products by the action of acids, but there is no experimental demonstration of the occurrence of this process in the biogenesis of condensed tannin extracts generally, and the approach would seem to be open to criticism. (see Hathway and Seakins *-loc. cit.*)[81b, c, d]

The Tea Tannins. The need for a less rigid approach to condensed tannin chemistry is perhaps best illustrated by recent work on the chemistry of the so-called tannins of tea, which not only brings the catechin hypothesis into proper perspective but also serves to illustrate the limitations of the leucoanthocyanidin concept dealt with later. A remarkable number of individual polyphenols has now been identified in the tea leaf, but none of those identified to date can be termed tannins. Gallic acid was found in green tea-leaf infusions by Hlasiwetz[96] and, owing to the extent of its occurrence, there was a tendency to group the tea tannins with the hydrolyzable tannins. The true position was revealed when Tsujimara[238, 239, 240, 241, 242] found that ethyl acetate extracts of Japanese green tea contained not only L-epicatechin but also L-gallocatechin and 3-galloyl-epicatechin.



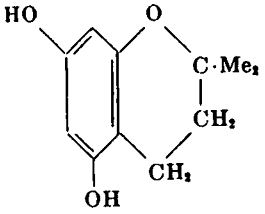
L-gallocatechin



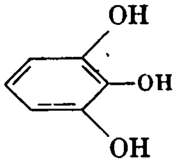
3-galloyl-epicatechin

These isolations of a catechin containing a pyrogallol group in place of the catechol of Freudenberg's catechin, and of a galloyl ester of a normal catechin, were obviously important.

Further progress came when Bradfield, Penney, and Wright[26] examined by partition chromatography on silica gel the 12 per cent yield of polyphenols obtained from Ceylon green tea by extracting a tea infusion with ethyl acetate. They obtained L-(−)-gallocatechin in 1.3 per cent yield and DL(+ −)gallocatechin or epicatechin in 0.6 per cent yield, and in the course of the work made the valuable observation that the ultraviolet absorption maximum of gallocatechin could be regarded as the sum of the maxima for a dihydroxy chroman and pyrogallol.



dihydroxy dimethyl chroman



pyrogallol

gallocatechin:
λ_{max} 271 $m\mu$. $E_{max} = 1{,}340$.

λ_{max} 272 $m\mu$. $E_{max} = 624$: λ_{max} 276 $m\mu$ $E_{max} = 800$: Total $E_{max} = 1{,}424$.

Bradfield and Penney[25] also isolated (−)epicatechin gallate in 0.9 per cent yield, (+ −)catechin in 0.1 per cent yield, a galloyl ester of a new gallocatechin in 0.5 per cent yield, (−)epicatechin in 0.5 per cent yield, and (−)gallocatechin gallate in 4.3 per cent yield—these five totaled 75 per cent of the initial extracted polyphenols or 8 per cent of the weight silver wattle *under the particular conditions of test.* Small amounts of cyanidin were formed from the extracts of wattle (*A. mollissima*), urunday, spruce, canaigre, and algaroba. It would seem, therefore, that the leucoanthocyanidin hypothesis is likely to be significant in the case of the eucalyptus and mangrove extracts but of less importance in the case of the remaining condensed tannins. It has been pointed out earlier how this high content of leucoanthocyanidins demarcates mangrove and eucalyptus extracts, while their content of catechin similarly demarcates Burma cutch and gambier extracts from the remaining condensed tannins.

The question was also examined whether or not quebracho and mimosa extracts contained significant amounts of structures capable of producing anthocyanidins, using not only the simple acid treatment described above but also the specific technique of oxidation with bromine in dioxane used by Appel and Robinson[3] to convert catechin to cyanidin, and the techniques of reducing with magnesium, hydrochloric acid, and mercury (Willstatter and Mallinson[258]), or with zinc and hydrochloric acid (Malkin and Nierenstein[138]) used to reduce quercetin to cyanidin. The reaction products were examined by paper chromatography and ultraviolet spectroscopy, but neither oxidation nor reduction provided any evidence of anthocyanidin formation from either quebracho or mimosa extracts, methylated or unmethylated, although parallel experiments with tetramethyl catechin and quercetin gave cyanidin without any difficulty. Since then, Roux[187a] observed that treatment of quebracho extract with HCl-propanol under pressure gave fisetinidin and suggested that corresponding leucoanthocyanin might be present in *S. lorentzii* heartwood. Later, [187b] he claimed that this reagent, and the use of p-toluene sulphonic acid as a diagnostic spray reagent for paper chromatograms, indicated "the presence of leucoanthocyanins in relatively high concentration in both wattle and quebracho extracts". This does not accord with the early findings of King and White[118] for the commercial extract, but the reaction conditions are not identical in the two sets of work and until Roux's quantitative data are published the true difference of findings cannot be assessed.

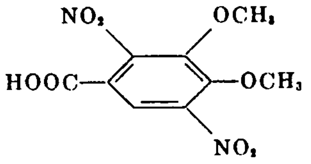
Simultaneously King and White[113b,c] made a comprehensive study of the polyphenol content of the fresh leaves, twigs, bark, sapwood and heartwood of the three quebracho species (*S. balansae*; *lorentzii*; ***heterophylla***) and showed that the sapwood contained significant amounts of a leucofisetinidin and a leucocyanidin. Both are absent (or present only as traces) from the commercial extract, having condensed up in the heartwood, but the former is clearly the source, albeit indirectly, of the fisetinidin observed by Roux.[187a] This however, is only a part of the story of the quebracho tannins—the fuller picture is detailed later.

The Forestal Concept. No true condensed tannin extract has yet yielded such a wealth of information about its components as the extract of tea, but in the case of both quebracho and wattle extracts considerable progress has now been made, and it can only be a matter of time before the nature of most of their components is known.

Quebracho extract achieved a position of major importance as a tanning material long before wattle extract, and Arata[4] obtained both phloroglucinol and protocatechuic acid by fusing quebracho extract with alkali. Nierenstein[149] obtained resorcinol and claimed that alkaline degradation of the brominated extract gave isovanillic acid (monomethyl protocatechuic acid) and that anthracene could be obtained by distilling the phlobaphenes with zinc dust. Perkin and Gunnell[160] identified as the flavonol fisetin a product first obtained by Arata, showed that gallic acid was present in the hydrolyzed extract, and suggested that ellagic acid might also be present; this, however, was incorrect.

Jablonski and Einbeck[99] and Einbeck and Jablonski[49] confirmed the existence of resorcinol nuclei in quebracho extract by isolating styphnic acid (trinitroresorcinol) in 9 per cent yield on oxidation with nitric acid. Later[50] they observed that the oxidation also produced a 5 to 10 per cent yield of 3,5-dinitro-β-resorcylic acid from the ethyl acetate soluble portion of the extract, showing that at least some of the resorcinol nuclei were linked by a meta-positioned carbon atom to whatever other structures were present. They failed to find any evidence of phloroglucinol but stated that since quebracho extract formed fluorescein on reacting with phthalic anhydride, whereas substances such as fisetin and morin, which had one hydroxyl of the resorcinol group occupied in an ether linkage, did not give the reaction, both resorcinol hydroxyl groups were free in quebracho tannin, which must therefore have a chalcone rather than a catechin structure.

Shortly before his death Dr. Jablonski sent the writer an unpublished thesis (1925, with W. Eggert) relating to the oxidation with chromic acid, nitric acid, and permanganate of methylated quebracho extract which he found surprisingly resistant to hydrolysis with alcoholic potassium hydroxide. Oxidation with chromic acid by the method of Grün and Wirth[76] gave a 20 per cent yield of veratric acid, while nitration followed by permanganate oxidation gave the previously unrecorded 2,5-dinitroveratric acid, melting point = 188–189°C.

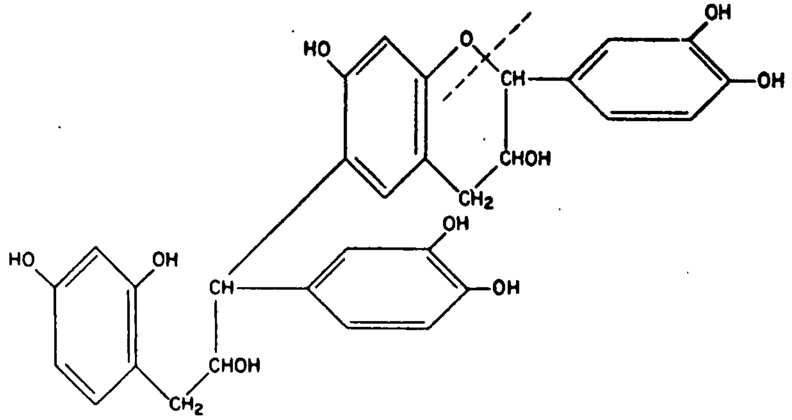


2,5-dinitroveratric acid

On the other hand, none of these degradations produced resorcinol derivatives from the methylated extract, and Dr. Jablonski concludes that the alkaline methylation conditions cause a ring closure involving a previously free resorcinol hydroxyl group.

The writer can confirm the high resistance of methylated quebracho extract to alkaline degradation, and alkaline oxidation of the unmethylated extract does cause its resorcinol reactivity to disappear even under conditions to which resorcinol itself is stable. This is true also of mimosa extract, and it seems important, therefore, to place on record the above unpublished work of Dr. Jablonski, although it must be emphasized that the results apply to a mixture of much greater complexity than he realized.

Up to this stage no attempt to put forward a formula for quebracho tannin had been made, although Korner[121] gave an analysis C = 62.5 to 62.74; H = 4.79 to 4.82. Freudenberg, Fikentscher, Harder, and Schmidt,[59] on the basis of the formation of resorcinol and protocatechuic acid by alkali fusion of the extract, postulated that quebracho tannin had a catechinlike structure with a hydroxyl distribution similar to that of fisetin. Freudenberg and Maitland[62, 63] specifically claimed quebracho extract to be a mixture of high-condensation products, all of similar structure, built by irreversible condensation of quebracho catechin which they synthesized but failed to find in the natural extract. They claimed that quebracho tannin was formed by pyran-ring opening of this quebracho catechin and subsequent elimination of the hydroxyl group so formed with the 6-position hydrogen of a second molecule to give polymerization by carbon-to-carbon linkage:



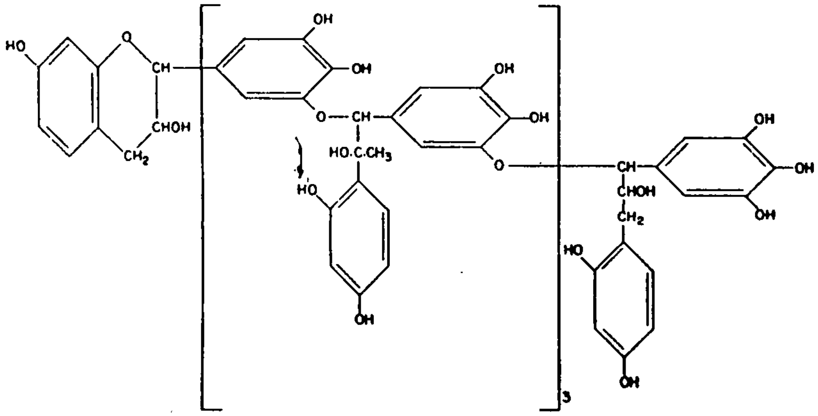
Their practical work was carried out on a "fraction B" which constituted about one-quarter of the normal extract (it is also the portion which contains the low-molecular-weight flavonoids, etc., of the extract).

A 9.4 per cent yield of resorcinol was obtained by alkali fusion of "fraction B," and a 25 per cent yield of veratric acid by potassium permanganate oxidation after methylation, but these facts cannot, in the light of modern work, be regarded as proving the polymer hypothesis put forward.

Little attention was paid to wattle extract at this time, but Einbeck and Jablonski[60] obtained styphnic acid and dinitro-β-resorcylic acid by nitric acid oxidation of the extract, and trimethyl-gallic acid and veratric acid by potassium permanganate oxidation of the methylated extract. Oxidation of the methylated extract with nitric acid followed by potassium permanganate gave 2,4-dinitroveratric acid, and again, as in the case of methylated quebracho extract, no resorcinol derivatives were formed.

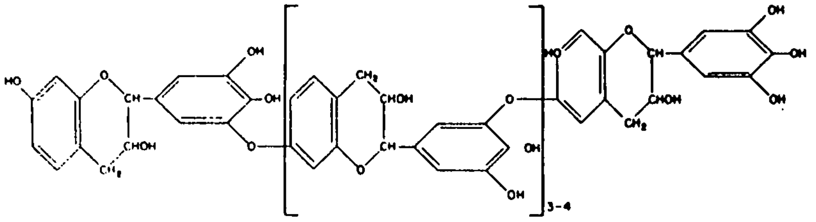
Subsequent published work up to 1949 (some even later) concentrated on explaining the chemistry of quebracho or wattle extracts in terms of a single tannin in each case. Studies of the particle size, diffusion, molecular weight, viscosity, and conductimetry of wattle extract by the Grahamstown Leather Industries Research Institute[131] up to 1944 are detailed in an institute publication of that date ("The Properties and Practical Application of Wattle Tannin," Grahamstown, 1944). Since the work involved what is now known to be a complex mixture, the results cannot be readily interpreted. On the organic side Stephen (page 135 of above text) concluded that wattle tannin had an empirical formula $C_{15}H_{13}O_6$ or $C_{15}H_{13}O_{6.5}$, and that two acetylated tannins could be obtained with 3.4 or 4.6 acetyl groups per C_{15} unit. Methylation introduced 31.5 to 33 per cent methoxyl, but an acetyl content of 7.6 per cent could be obtained by acetylating these products, indicating the methylation to be incomplete. Alkali fusion of the initial tannin produced resorcinol, while potassium permanganate oxidation of the methylated product gave veratric acid and trimethyl gallic acid, confirming Einbeck and Jablonski's[60] finding that the extract contained both catechol and pyrogallol nuclei. Stephen also noted that wattle extract oxidized in alkali solution with the formation of acidic carboxyl groups.

Kirby[114] (see Catravas and Kirby[37]) carried out similar oxidations of methylated fractions of wattle extract and confirmed the presence of methylated catechol and pyrogallol nuclei. Resorcinol derivatives were obtained only from the unmethylated extract, except for one oxidation of a methylated product with nitric acid which was claimed to produce 2,4-dimethoxy-5-nitrobenzoic acid. This was taken as suggesting that resorcinol existed in the extract with both hydroxyls free. Kirby also claimed to have separated two methylated products from the extract, one of which gave only trimethyl gallic acid on oxidation, whereas the other gave only veratric acid, but Roux[183] failed to confirm this, all his repetitions giving a mixture of both acids. Kirby suggested for his main tannin fraction a pentameric formula based on the catechin hypothesis, but the suggestion is now of historical interest only.



Meanwhile, Williams[257] and Heugh,[85] followed by Roux,[182] concentrated on purifying wattle tannin using hide-powder analysis and element analysis as the criteria of purity, and elution of adsorbed tannin, precipitation as the lead salt, solvent extraction, salting out, or combinations of these techniques as the methods of isolation. The work seems to have been based on the idea that wattle tannin could be obtained pure enough for an empirical or structural formula to have meaning, although the tannin was at the same time stated to be a mixture.

Roux[183] gave a useful summary of earlier work but, on the basis of the Freudenberg catechin hypothesis, concluded that the unit of wattle tannin was a 3,7,3′,4′,5′-pentahydroxy-2-phenyl chromane of empirical formula $C_{15}H_{13\text{ or }14}O_{6}$. Acetylation of his material gave a product with 37.48 to 38.32 per cent acetyl, and methylation introduced 36.8 per cent methoxyl, corresponding to four hydroxyl per C_{15} unit. He assumed from previous Grahamstown work that wattle tannin had a molecular weight of the order of 1,500 to 1,800 and stated, "The tannin molecule is thus either one large highly complex unit or else a polymer of a single unit," giving as a formula



He stated that the formula was an average one which "does not exclude the possibility either of minor variations in terminal groups—or even minor variations in structural units," but it is clear that up to this stage the real complexity of wattle tannin extract, like that of other condensed tannin extracts, was not realized. A similar comment applies to the attempts of Buchanan, Lewis, and Weber[30] to prepare "purified" tannins, using the hide-powder analysis as the only criterion of purity, and to the attempt of Shuttleworth[219] to compress the chemistry of quebracho extract into a single structural formula. He suggested that quebracho tannin is a polymer of a catechin and that polymerization took place by hydrogen bonding, but the formula suggested (and its two variants) involves hydrogen bonding from the hydrogen atoms of the benzene rings, a form of hydrogen bonding which is improbable and probably nonexistent.

The idea that a single formula could explain the chemistry of the complex mixture of different polyphenols present in each condensed tannin extract had to be discarded after the reviewer White[252] published the first of a series of communications detailing the results of applying modern physicochemical and organic techniques to tannin chemistry. The work demonstrated the great complexity of composition of tannin extracts in general, and provided methods of separating and characterizing the individual substances in each extract.

White, Kirby, and Knowles[256] later summed up the approach in the words, "Our investigations were begun with the conviction that elucidation of the chemistry and behaviour of any tannin extract requires consideration of all the extract, not just of part of the initial material isolated by an arbitrary method of purification and considered without reference to the remainder. ... The fact that tannin extracts consist of mixtures of large numbers of substances, with polyphenols predominating, seems to be one of the primary factors governing the chemical and physical behaviour of the extracts."

The first paper of the series applied the Northrop and Kunitz[162] solubility-curve method and also single-way paper chromatography to quebracho extract. The solubility curves showed that the extract could be distinguished by these techniques into five major components, but the paper chromatographic work showed that two at least of these were themselves complex and far from homogeneous. By combining paper chromatography and examination in ultraviolet light, the characteristic yellow fluorescence of the extract, previously believed to be due to fisetin, was found to be due to at least 8 different yellow fluorescing substances, and these early single-way paper chromatograms showed that the extract contained not less than 14 substances.

Kirby, Knowles, and White[115] applied single-way paper chromatography to a wide range of hydrolyzable and condensed tannin extracts and showed that a high degree of complexity existed in all the material examined. Hillis[86, 87, 88] simultaneously and independently followed the same approach, and came to the same conclusion that tannin extracts were far more complex in composition than earlier workers had realized.

This was demonstrated beyond doubt when White, Kirby, and Knowles[256] described the results of investigating a large number of extracts by two-way paper chromatography and by the Craig[40] technique of partition between immiscible solvents. They showed that this latter technique could produce good fractionation of mimosa extract on a reasonable scale of working, that two-way paper chromatography could resolve and characterize most of the individual components of a tannin extract, and that by combining the two methods fractionation could be achieved and followed in minute detail. It thus became possible for the first time to characterize and separate *any* of the individual components of tannin extracts and to provide reliable criteria of purity for them. This paper also showed that one of the major factors which had previously prevented easy purification of the individual components of condensed tannin extracts in particular was that these extracts exhibited a high degree of mutual component solubilization or peptizing, and tended to form solid solutions which are difficult to examine by normal means. A second factor which was emphasized was that, because so many of the components were characterized mainly by their possession of numerous phenolic groups, the over-all phenolic reactivity tended to outweigh minor differences of behavior, again making characterization and separation difficult.

Having established this general picture of natural tannin extracts, Kirby, Knowles, and White[116, 117] and Kirby and White[118, 119] applied various methods of fractionating quebracho and wattle extracts, following them by two-way paper chromatography, and showed that wattle extract contained at least 27 polyphenolic substances and a further 10 fluorescent substances, while quebracho extract was even more complex. The later papers commenced the task of isolating individual components, and, in the case of quebracho extract, the following substances are now known to exist in the extract in the free condition: anthraquinone, gallic acid, glucose, galactose, xylose, rhamnose, arabinose, ribose, fucose, robinetin, fisetin, fisetin-4-methyl ether, and 3,7,4′-trihydroxyflavone, together with at least 12 other yellow-fluorescing flavonoid substances which are hydrolyzable derivatives of the four flavonols concluding the above list. The nature of 25 components of the extract is therefore known exactly or sufficiently well to state their general structures. Since these 25 substances form only about 5 per cent of the whole extract, the complexity of composition of the latter is evident.

The structural relationship of the four primary yellow-fluorescing flavones recalls the similar mono-, di-, and trihydroxybenzene relationship

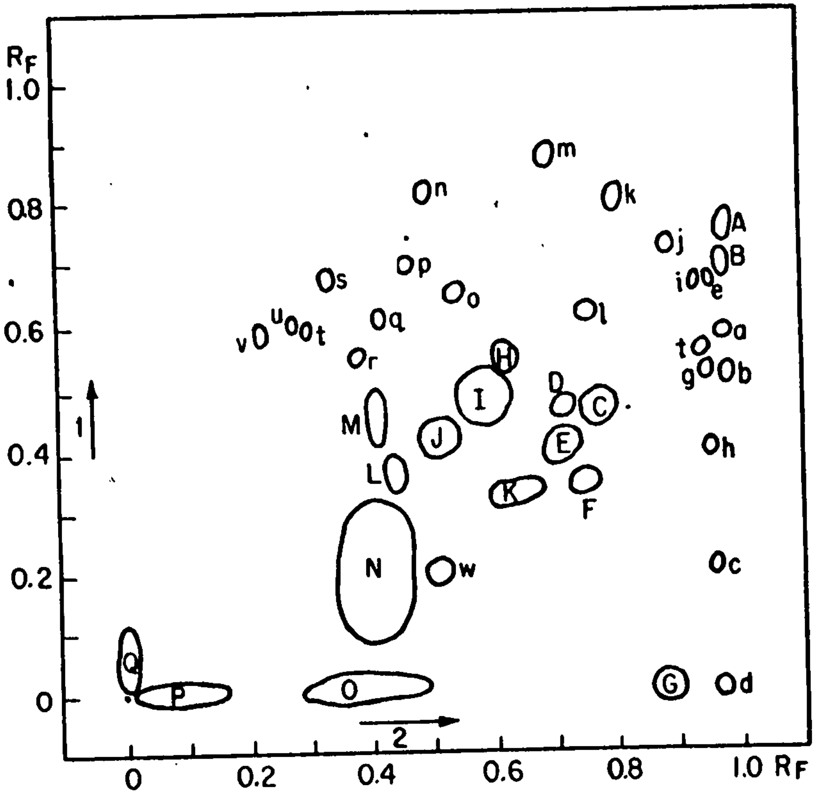


FIG. 18-3. Composite diagram of 2 Way chromatograms of quebracho extract and fractions showing location of phenolic components.

From Kirby, K. S., Knowles, E., and White, T., J. Soc. Leather Trades Chemistry, 37, 283 (1953).

known in the anthocyanidins and in the aldehydic oxidation products of lignin (*p*-hydroxybenzaldehyde; vanillin; syringic aldehyde). This relationship is of considerable interest in the light of the later study by King and White[113b,c] of the polyphenol content of the leaves, young twigs, bark, sapwood and heartwood of the three species of *Schinopsis* (quebracho), i.e. *balansae*, *lorentzii* and *heterophylla*. This study throws considerable light, for the first time, on the genesis of the quebracho condensed tannins and has demonstrated a previously unsuspected relationship to the hydrolyzable tannins in the *Schinopsis* genus and throughout the *Anacardiaceae*. The leaves of the three species were found to produce a variety of phenolic components identical with, (e.g. chebulic acid, corilagin, chebulagic acid, ellagic acid, gallic acid) or similar to, (e.g. a gallotannin) many already known as components of typical hydrolyzable tannins such as myrobalans extract or tannic acid. No condensed tannins or C_{15} components seemed to be present in the leaves despite their known predominance in the heartwood, the only other identifiable polyphenols in the leaves being a variety of quinic acid derivatives (e.g. chlorogenic acid, neochlorogenic acid, p-coumaryl quinic acid and theogallin and neotheogallin) whose occurrence here in association with hydrolyzable tannins is particularly significant in the light of the suggestion already outlined that these substances participate in the metabolic path leading to the gallotannins.

The barks were found to act as storage centers for these quinic acid derivatives and, in addition to traces of the hydrolyzable tannin components, also contained traces of *d*-catechin. The sapwood showed a significant content of gallic acid, the gallotannin and two other hydrolyzable galloyl derivatives derived from the leaves, and was also found to contain *d*-catechin and a leucofisetinidin and leucocyanidin as its remaining primary phenolic components together with lesser amounts of fustin (dihydrofisetin) and other dihydroflavonols, with the primary flavones mentioned above.

These components increased in amount as the sapwood-heartwood boundary was approached, and at that boundary the hydrolyzable components disappeared suddenly while, a little way inside it, the *d*-catechin and the two leucoanthocyanins also disappear. In the heartwood proper the still unidentified condensed tannin molecules are accompanied by the numerous yellow fluorescing flavonols described above, by traces of the three dihydroflavonols of the sapwood, and by two hydroxy-coumaranones showing an interesting biogenetic relationship to fisetin and methoxy fisetin. This type of substance has not been recorded naturally before.

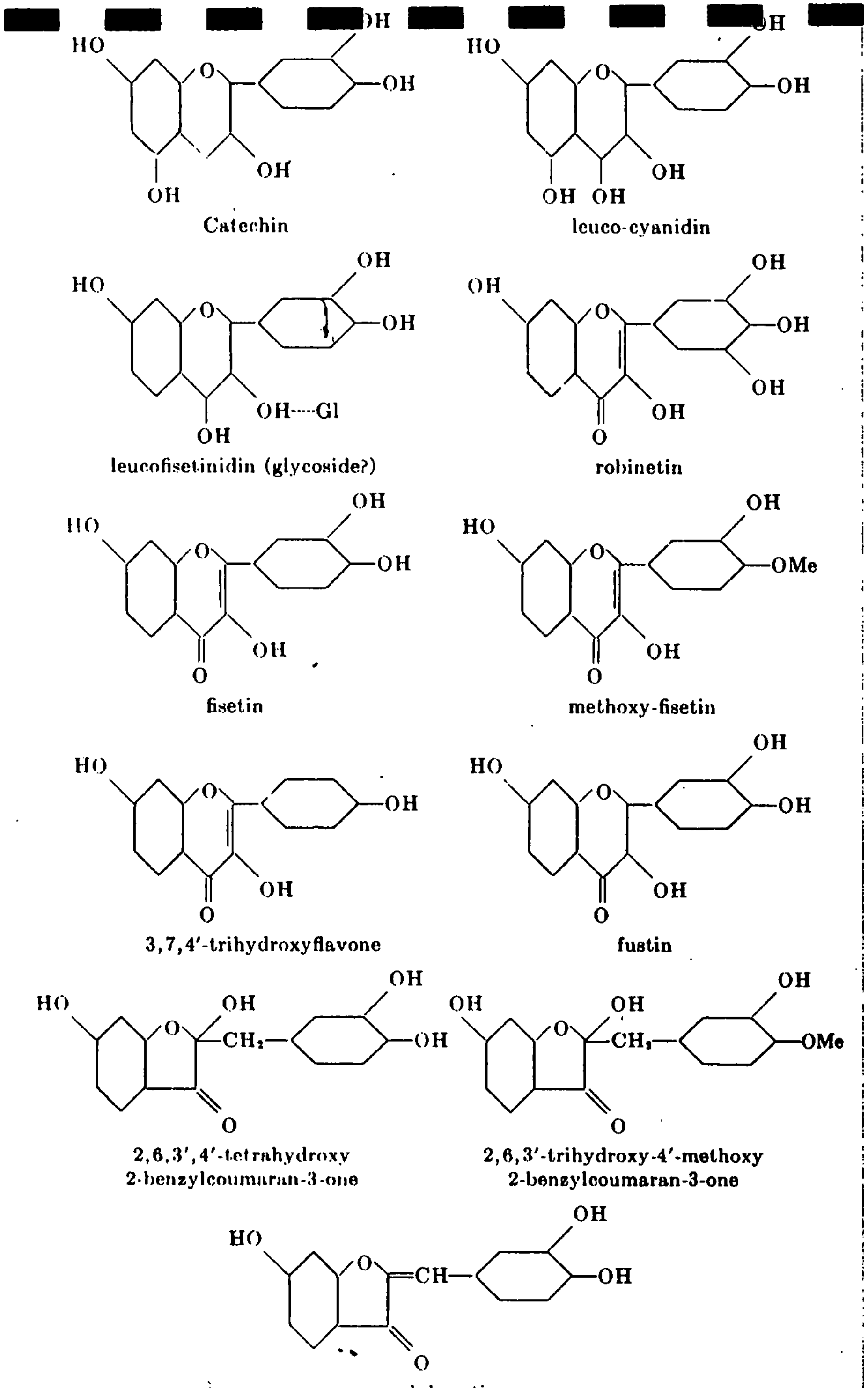
The overall picture is clearly one of synthesis of hydrolyzable tannin components in the leaves (via the quinic-shikimic acid route?)—transport of these substances to the sapwood, with *d*-catechin and leucoanthocyanins arising en route, possibly in the cambial layer by processes which may utilize the galloyl residues of the hydrolyzable tannins as precursor residues. At the sapwood-heartwood boundary all these substances participate in formation of the typical heartwood condensed tannins of the quebracho tree, entering into mutual mixed condensation possibly under the influence of polyphenoloxidases along the lines suggested by Hathway and Seakins[81b,c,d] for *d*-catechin in Burma cutch. Here indeed lies the reason for the complexity of the condensed tannins of quebracho extract. Both the catechin and leucoanthocyanin hypotheses of condensed tannin formation can now be viewed in proper perspective as far as quebracho is concerned. Both types of substance participate in formation of the quebracho tannins, but so too do the hydrolyzable galloyl derivatives derived from the initial leaf metabolism. There is equally no reason to exclude the dihydroflavonols, and the two hydroxy-coumaranones also detected, from ultimate participation in whatever reactions these monomeric substances undergo in forming the higher molecular weight polymers we regard as tannins. Most of these latter probably come in the range of dimers to pentamers and Roux's[187a] liberation of fisetinidin from quebracho extract by acid treatment merely indicates that such leucoanthocyanin nuclei as are linked into the polymers are so joined that some at least can still give rise to anthocyanidin on appropriate treatment.

The fact that all these substances are biogenetically related and stem from probably a single metabolic route is probably best illustrated by the diagram of their structural formulae in Figure 4. Particular attention should be directed to the similarity of hydroxylation pattern and to the striking relationship between fisetin and methoxy fisetin and the corresponding pair of hydroxy and hydroxy-methoxy coumaranones.

This series of communications initated a changed approach to the problem of tannin chemistry. The value of paper chromatography as a technique in this field, as well as the better realization of the complexity of the extracts, is well evidenced in the recent papers by Schmidt and Lademann,[211] Hillis,[86, 88, 89, 90, 91] Roux,[185, 186] Asquith,[5, 6] Roberts and Wood,[175, 176, 177] Cartwright and Roberts,[34, 35] Oshima, Nakabayashi, Hada, and Matuyama,[154] and Nakabayashi and Hada,[146] most of which are dealt with separately in this survey.

These communications represent the majority of publications along this line to date. They amply confirm the thesis of the writer and his colleagues that tannin extracts are highly complex mixtures and that, unless this is realized and allowed for, degradative and structural organic work is meaningless. In the case of wattle extract, Roux[186] has since demonstrated by paper chromatography that the ether-soluble portion of the extract contains traces of catechin, a gallocatechin, gallic acid, fisetin, and possibly resorcinol. King,[112] King and White,[113] and White[253, 254] have also recorded these substances and added epicatechin, syringic acid, traces of leucoanthocyanidins capable of conversion to cyanidin, delphinidin and pelargonidin, fisetin, robinetin, and 3,7,4′-trihydroxyflavone in the extract, thus establishing the same mono-, di-, trihydroxy relationship of the flavonols as in quebracho extract. Catechin is present to only 0.02 per cent of the whole extract, so that it is hardly of major importance.

Roux[185] also applied paper chromatography to the problem of identifying the products of alkali fusion of degummed wattle extract—the material used containing all the main polyphenolic tannins of the extract. In addition to obtaining yields of 11 per cent of gallic acid and 10.5 per cent of resorcinol, both previously reported, he also established a 4.2 per cent yield


Catechin

leuco-cyanidin

leucofisetinidin (glycoside?)

robinetin

fisetin

methoxy-fisetin

3,7,4′-trihydroxyflavone

fustin

2,6,3′,4′-tetrahydroxy 2-benzylcoumaran-3-one

2,6,3′-trihydroxy-4′-methoxy 2-benzylcoumaran-3-one

sulphuretin

FIG. 18-4. Structural inter-relationship of C_{15} components of *S. balansae* sapwood and heartwood.

of β-resorcylic acid, 1 per cent of pyrogallol, and traces of phloroglucinol and protocatechuic acid, none of which had been previously reported. Putnam and Rockett[172] similarly identified β-resorcylic acid in the products of alkali fusion of quebracho extract. Roux also obtained by potassium permanganate oxidation of methylated wattle extract a 25 per cent yield of a mixture of veratric and trimethyl gallic acids, and again confirmed that no resorcinol derivative could be obtained from the methylated extract. He pointed out that the alkali fusion of the initial extract yielded approximately equal quantities of resorcinol and of catechol plus pyrogallol, and regarded this as evidence of the presence of $C_6 \cdot C_3 \cdot C_6$ compounds. He stated that the yields of veratric acid plus trimethyl gallic acid are comparable with those from D-catechin, showing that after methylation the catechol and pyrogallol nuclei are free and attached to a single carbon only. They could not therefore be participants in condensation reactions as previously suggested by Roux[183] or Catravas and Kirby.[37]

It is still not possible to say much more about the detailed structure of the true tannins of either quebracho or wattle extracts at present is that they are undoubtedly built mainly of catechol, pyrogallol, resorcinol, and possibly *p*-hydroxyphenol and phloroglucinol residues with the origin of these nuclei in the quebracho tannins now clear from the work of King and White. In the most homogeneous tannin-containing fractions of quebracho extract so far examined by Kirby and White,[118] examination of the ultraviolet spectra showed that approximately half the oxygen atoms in this mixture of tannins are occupied in ether linkages, the majority of the remainder being present as phenolic hydroxyls with 15 per cent of the total oxygen atoms seeming to have an aliphatic hydroxyl character. The substances involved seem to have molecular weights of the order of 600 to 700, and Putnam and Gensler[169] quote similar low values for a quebracho extract fraction which they mistakenly believed was a single substance. As will be seen later, Roux[186] believes the tannins of wattle extract to possess molecular weights of the order of 950, and Evelyn[51] has since confirmed this experimentally.*

These values are far from the colloids of other workers and give little, if any, support to the idea that natural tannin molecules are high polymers. Even if the catechin hypothesis were correct, it would be mainly dimers to tetramers that would be involved. As yet, however, it is only safe to say that the tannin molecules of quebracho and wattle extracts contain sufficient phenolic nuclei to allow of a fair degree of structural variation, and the mode of attachment of these nuclei to each other is still unknown. The existence of variation is, however, amply vouched for by paper chromatography.

It remains only to deal with a series of papers which could not logically

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* Added in proof. See Evelyn, *J. Soc. Leather Tr. Chem.* **40**, 335 (1956).

be fitted into the above discussion. Putnam and Gensler,[169] Putnam and Bowles,[167] and Putnam[165] claimed to have isolated as much as 67 per cent of quebracho extract as a pure substance. They acetylated this product with pyridine and acetic anhydride and then further treated it with acetyl chloride and dimethylaniline. They termed this latter treatment a "peracetylation" and claimed that it opened up any oxygen linkages in their quebracho tannin and resulted in acetylation of every oxygen atom in the molecule. In support of this they gave an analysis for their acetylated product indicating it to contain 46 per cent acetyl, whereas no other worker has been able to introduce more than 38 to 39 per cent acetyl into any product derived from the extract. They claimed the empirical formula of quebracho tannin to be $C_{31}H_{18}O_{11}$ and the acetate to be an undeca-acetate containing 11 acetyl groups.

Putnam and Gensler[170] and Putnam[165] then made a similar claim to have acetylated all the oxygen atoms in "pure" wattle tannin by a similar peracetylation technique and formulated the relevant acetate as a dodecacetate containing 12 acetyl groups. Putnam[165] and Putnam and Bowles[168] made similar claims to have peracetylated mangrove tannin and acetylated all the oxygen atoms to form a dodeca-acetate.

In none of these cases is an analysis given for the acetyl content at the end of the first acetylation with pyridine and acetic anhydride, and before the so-called "peracetylation." In each case the method of obtaining a "pure" tannin is the solvent extraction technique of Buchanan, Lewis, and Weber.[80]

In view of the claims made, the papers cannot be left without comment. Kirby and White[118] repeated the described preparation of the "pure" quebracho tannin and found by two-way paper chromatography that it contained all the main polyphenolic substances normally present in the extract, so that the material is not a pure substance. They repeated the double acetylation procedure and obtained the normal acetyl values of 38 to 39 per cent at the end of both the first and second stages of acetylation—so that no evidence of peracetylation could be found.* They also compared the spectra of these derivatives with those of test substances and concluded that a high proportion of the oxygen atoms in the acetylated material were still engaged in ether linkages which the acetylation procedure had not opened.

Roux[186] similarly chromatographed a sample of "pure" wattle tannin provided by Putnam and also found it contained all the main wattle polyphenols, so that it was far from pure. He too repeated the double acetylation procedure and found a normal acetyl value at the end of the first stage of acetylation, and no increase on applying the so-called "peracetylation" procedure. Both groups of workers therefore independently concluded that the Putnam claims were based on incorrect acetyl analyses.[187]

The American workers themselves point out that D-catechin and their initial unacetylated "pure" tannin gave up to 8.8 per cent acetyl content when tested as blanks in their method of acetyl determination, but Putnam and Bowles[167] state, "We can see no way in which the acetyl values of the acetylated tannins can be reliably corrected for apparent acetyl contents of the unacetylated tannins." When their "pure" tannin were first methylated and then acetylated, the acetyl values for the acetylated-methylated products were then normal and, with the methoxyl values, indicated the same number of hydroxyl groups as other workers have found. This suggests that the factor causing high values in the case of their acetylated tannins is alkaline oxidative rupture of the catechol and pyrogallol nuclei, which, of course, does not occur once the hydroxyls have been protected by methylation.

Putnam, O'Gorman, and Bowles[171] have again claimed their acetyl determinations as correct but have not commented on the published evidence that their "pure" products are mixtures, and that the so-called "peracetylation" has been found not to increase the acetyl value above that achieved by normal acetylation. Under the circumstances, it is difficult to accept the findings in this series of papers.

Bisulfiting. In view of the practical importance to the leather industry of sulfite-bisulfite solubilized quebracho extract, it is necessary to summarize here the investigations of this process which have so far been published.

Quebracho extract is made by hot-water extraction of tannin-containing heartwood and contains a proportion of so-called "phlobaphenes" which are insoluble in cold water. In order to make these available for tannage, solubilizing sulfonic acid groups are introduced by treating with sodium sulfite and/or bisulfite, a method first disclosed by Lepetit, Dollfuss, and Gansser.[133] The practical aspects are covered by Vogel[247]

Lepetit[132] showed that the sulfonic groups became part of the extract structure since they were not removed by simple acidification, and that some of the introduced sulfur dioxide existed as carbon-bound sulfur. Stiasny and Orth[228] postulated that the solubilizing procedure dispersed colloidal extract particles, converting part of the tannins into nontannins, although the total tannin content increased owing to dissolution of the phlobaphenes.

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* An authentic "peracetate" provided by Dr. Putnam to the writer also gave the normal acetyl value when analyzed by the writer's laboratory and independently by Weiler and Strauss, Oxford.

sole leather is equal in all respects and superior in some to the older, long-time, tannages of the past century." Stather[89] reaches similar conclusions.

That critics are chronically incapable of viewing the past except through rose-tinted spectacles, is confirmed by Harrison's lament:[29] "Only this I wish that our sole and upper leathering may have their due time, and not be hastened by extraordinary slights, as with ash bark, etc. Whereby as I grant that it seemeth outwardly to be very thick and well done; so, if you respect the sadness [i.e., solidity] thereof, it doth prove in the end to be very hollow and not able to hold out water."

On the other hand, not all the "improvements" are quite as modern as most of us would like to believe, for the Preamble to the Acts of Edward VI (1537–1553) for the tanning of leather[62] reads: "Whereas in times past the hides or leather were wont to lie in the tan vats by the space of one year or five quarters of the year, before it was taken out of the same vats or put to sale, now for the speedy utterance and tanning thereof they have invented diverse and sundry deceitful and crafty means to have the same leather tanned, some time in three weeks and some time in one month or six weeks at the most." Among those "sundry deceitful and crafty means" were: "Putting seething hot liquor with their oozes into their tan vats, which they most commonly do practice in the night time."

For the above references, the writer is indebted to Mr. F. E. Artz.[2]

VEGETABLE TANNING MATERIALS AND THEIR PROPERTIES

Practically all wood or shrubby vegetation contains some form of tannin, present in the wood, bark, leaves, twigs, fruits, pods, galls, or roots. In addition to a list compiled by Wilson and Thomas,[110] Happich, Beebe, and Rogers[28] evaluated 163 species. According to Harvey,[30] the International Commission for Plant Raw Materials' publication "Materiae Vegetabiles" summarizes the data on the genus *Caesalpinia* and may well cover other species in later volumes. However, only a relatively few materials are of immediate and commercial importance in the United States. A review of the chemical properties of the 26 tanning materials of interest in Great Britain has been given.[48] Howes[34] has published an excellent book on the subject, to which the reader is referred.

While not the ideal method of classifying the types of tanning materials, it is probably sufficient from the leathermaking standpoint to divide them into two broad groups, the catechols and the pyrogallols, depending on whether catechol or pyrogallol is yielded on fusion with alkali. While the chemistry of the vegetable tannins has been dealt with in the preceding chapter, from the practical standpoint the catechol tannins generally contain very little acid or sugars and give reddish leathers; their solutions are usually very sensitive to pH, giving a precipitate of phlobaphenes or "reds" on acidification. Conversely, the pyrogallols are usually quite acidic,[5, 84] contain fairly large amounts of sugars, and generally are less sensitive to lowering of pH. However, they tend to deposit "bloom" as a result of the action of enzymes native to the original source (bark, etc.).[85]

Catechol Materials. ***Quebracho.*** Quebracho tannin occurs in the wood of a tree indigenous to South America and more or less restricted to the northern provinces of Argentina and the southern provinces of Paraguay and Brazil—the Chaco region. Two varieties make up the bulk of the commercial production for tanning: Quebracho colorado chaqueño (*Schinopsis balansae*) and Quebracho colorado santiagueño (*Schinopsis lorentzii*). The wood is extremely hard (12.9 Brinell units) and heavy (specific gravity 1.2).[53]

Most of the tannin is extracted in Argentina and Paraguay, the leach (autoclave) liquor being settled, evaporated, and shipped as a solid extract. The ordinary quebracho extract, so produced, will show about 18 to 20 per cent of water, 5 to 8 per cent insolubles, and 63 to 64 per cent tannin, when analyzed by the official methods of the American Leather Chemists' Association. Used as such, the insolubles largely remain in solution at concentrations above 80 to 100° Bk (specific gravity = (1,000 +°Bk)/1,000), but rapidly settle out from weaker solutions. The tannin is astringent, penetrates relatively slowly, and gives a full and fairly firm leather of a reddish color. The color deepens markedly on exposure to light.

Both to speed up the rate of penetration and to overcome the tendency to excessive sludge formation, most tanners dissolve the extract in about an equal weight of hot water or weak liquor and digest for 24 to 48 hr with from 3 to 5 per cent of sodium metabisulfite. [Sodium sulfite, sodium bisulfite (liquid), and mixtures of these are also used.] Such treatment reduces the insolubles to less than 1 per cent, and these are of a much cleaner and less sticky nature. Analytically, the insolubles appear to be converted into tannin but, as one tanner puts it "you can't produce an extra pound of leather from that extra tan." The work of Pound and Quinn[66] and of Stuewe and Lollar[91] strongly suggests that the treatment breaks down the molecules of the tannin as well as those of the insolubles, so that less weight is obtained per pound of analytical tannin—thereby confirming the tanner's comment. The work of Turley and his colleagues[99] should also be consulted.

The sulfited quebracho is much less astringent, penetrates very rapidly, and gives a soft, empty, leather of a pale pink color which, however, also reddens on exposure to light. The treated extract is much more resistant to pH and even has a dispersing action on insolubles deriving from other materials present in the blend. For use in the "scrubhouse," where an even lighter color and greater dispersing action are desired, the extract will be treated with from 7 to 10 per cent of metabisulfite; in England, bleaching extracts are treated with up to 20 per cent of bisulfite or its equivalent. As shown by Pound and Quinn,[66] and confirmed by practical experience, increased treatment gives lower leather yields and lower fixation. It is the writer's experience that, properly used, 3 to 5 per cent of metabisulfite gives the maximum tannin value by the analytical method; further additions increase the nontannin value.

Occurring along with, and very similar to, the above species of quebracho is the urunday (*Astronium balansae*). According to Vogel,[101] the tannin is very similar to the two quebrachos but much darker in color, and is little used as a leathermaking material.

Wattle. Wattle tannin occurs in the bark of various species of *Acacia* (*Mimosa*) indigenous to Australia, but it is now grown commercially largely in South and East Africa, where the black wattle (*Acacia mollissima*) is the main source. Increasing amounts of the bark are being converted into solid extracts and shipped as such, but quite a little is still shipped as the bark and leached by the tanner. While a catechol tannin in many respects, wattle is not typical, as it is much less astringent, contains a fair quantity of sugars and nontannins (lower purity), and does not usually deposit much insolubles. A typical extract will analyze 62 to 63 per cent tans and 18 to 20 per cent nontans. Penetration is comparatively rapid. The color of the leather is a pale pink but, to the writer's eye, generally shows an undesirable gray cast which can be quite noticeable in the tannery. The iron content is generally very low (30 to 40 ppm on the solid extract), and the gray cast can be prevented (skiver color test) by the use of large (and uneconomic) amounts of the sequestering agent ethylenediaminetetraacetic acid or its salts. The writer suspects that the gray is due to the wattle molecule forming intensely colored complexes with the small amounts of iron present.

Treatment of the extract with small amounts of metabisulfite or, especially, of hydrosulfite ($Na_2S_2O_4$) bleaches the color markedly; with the latter reagent, an almost white (though not lightfast) leather can be produced.[111] Such bleaching does not affect the gray cast mentioned above.

The resistance of wattle to lowering of pH was taken advantage of by British tanners who found that suitable acidification of this extract with citric acid produced a very excellent replacement for the chestnut, which was unavailable during World War II.

Mangrove. Mangrove tannin occurs in the bark of various species of mangrove (*Rhizophora*). Most production is from Borneo, though some is produced in East Africa. Whereas the former gives a reddish-brown color on skiver and a fairly great tendency to sludge formation, the few samples of the latter examined by the writer appear to be redder (less brown) and clearer, with only a small deposition of insolubles. Treatment with bisulfite (1 to 2 per cent metabisulfite) renders both more stable to lowering of pH and brightens the color, the Borneo extract tending to be bleached. The Borneo material is shipped both as the bark and as a solid extract, both showing a high percentage of ash, deriving mainly from the chlorides of sodium and magnesium. The East African samples examined by the writer have been in the form of spray-dried powder, and showed a similar amount and type of ash.

The Borneo material is often called Borneo cutch, but it should not be confused with the true cutch, which is derived from a species of acacia (*Acacia catechu*). As a tanning material, mangrove penetrates very slowly but gives a firm, deep-colored, solid leather of good yield and high degree of tannage. Because of the slow penetration and its tendency to form a sticky sludge (except when bisulfited), it is generally used only in small proportion in a blend (10 to 20 per cent). The writer has no information on the actual leathermaking characteristics of the East African material.

Hemlock. Hemlock tannin occurs in the bark of a North American tree (*Tsuga canadensis*) and, at one time, furnished the major, often only, source of tannin for the United States tanner. Some is still available locally, particularly in connection with lumbering and papermaking in Michigan, Minnesota, and Wisconsin.[73] While some bark is shipped, it is believed that the greater part is made into a liquid extract of 25 per cent tannin content. With the growing scarcity of domestic tanning materials, attempts have been made to use the bark of the related western hemlock (*Tsuga heterophylla*).[64, 82]

Because of its unusually high acidity (for a catechol tannin), hemlock could be, and was, used as the sole tanning material and gave a firm, dark-red, leather. Rate of penetration was fairly good. It was considered particularly desirable for the production of "loggers oak" leather which must be able to hold the lumberman's calks while worn in water.

Eucalyptus. Practically all members of this species, growing mainly in Australia, contain worth-while amounts of tannin and are exploited on a sizable scale, and a solid extract is now on the market. Opinion as to the value of the extract seems to be divided; although it appears to give leather of satisfactory character, the color is of a dirty, purplish cast, and some samples of the extract give a sticky, dirty sludge. Neither the sludge nor the color is improved by any treatment known to the writer; bisulfite seems to make matters worse. It is possible that improved methods of collecting the bark, the selection of single species, and improved methods of manufacturing the extract would give a better material, more responsive to treatment with bisulfite; the writer understands that recent samples of the extract are already superior to those he examined. Chambard[13] and Chambard and Abadie[14] have investigated the use of the tannin of *Eucalyptus sideroxylon*, with special reference to its growth as a crop in French territories in North Africa.

Cutch. Cutch tannin is derived from the heartwood of *Acacia catechu*, common in India, Pakistan, and Burma. It is usually leached and concentrated to a solid extract, often by crude methods. According to Howes,[34] cutch gives a harsh leather, often with a yellow stain, and is not regarded as satisfactory; it is sometimes used on heavy leathers where a dark, reddish-brown color is desired. Its main use is as a preservative for fishing nets, sails, tents, etc., which it does very satisfactorily, giving the goods a fast, brown color. According to Procter,[68] good cutch contains 60 per cent tannin and is principally used for dyeing browns and blacks with chrome and iron mordants.

Gambier. Gambier tannin is obtained from the twigs and leaves of an East Indian shrub (*Nauclea* or *Uncaria gambir*). These are leached and the tannin is converted into a solid extract at the site, often by crude methods. The product comes to market in the form of large blocks or small cubes. The blocks are likely to be adulterated with twigs, leaves, etc., but the cubes are usually free of such gross impurities. Plantation gambier, prepared under more careful conditions, is usually of good quality. Since gambier is also used in the East as a masticatory, especially with betel,[34] 10 to 25 per cent of rice bran is often added to the native product as an aid to easier chewing. The extract contains a good deal of catechin, which acquires tanning properties only on being boiled. Gambier, used alone, gives a soft, spongy leather, as it has a fairly high pH value and total salts content, the greater part of which are the salts of weak acids. Used in blends, it has a mellowing effect owing to its low astringency, and this same characteristic makes it a useful mordant. It is very valuable for leathers requiring high tensile strength.

Pyrogallol Materials. *Chestnut.* Chestnut tannin occurs in the wood of the American chestnut tree (*Castanea dentata*). At one time, this tree grew abundantly in the eastern section of the United States, from New York and Pennsylvania south to Virginia, North Carolina, and northern Georgia and Alabama, and was used as a source of lumber. The scrap and smaller trees were the source of the tannin. The leaching was done either directly by the tanner or, more frequently, by the papermaker, who usually shipped it as a liquid extract of 25 to 30 per cent tannin.

Since the tree sprouts from the stump, a chestnut forest quickly replaced itself. However, around the year 1900, the chestnut-blight fungus (*Endothia parasitica*) came in from the Orient and has proved fatal; although sprouts still appear, they generally succumb to the blight at, or before, bearing age. Resistant crosses with Asiatic species have been made, but whether or not sufficient numbers can be planted is problematical. On the other hand, some of the native sprouts do bear fruit, and it is not impossible that some of these will become resistant by natural selection, as must have happened in the case of the Asiatic species. Lumbering, papermaking, and extract manufacture were continued using the dead trees but, with time, the quality and yield of tannin declined, and in 1956 only one small producer was known to be operating.

The extract was fairly astringent, of high purity, and penetrated fairly slowly. The leather was firm and well filled, and of a brownish-yellow color. Owing largely to the use of copper autoclaves and evaporators, the copper content was usually high, the better grades showing 250 to 300 ppm on the dry basis, and others running up to 1,100 ppm.

With the disappearance of the domestic chestnut, the United States tanner has turned to the European suppliers, whose extract derives largely from the related *Castanea vesca* or *Castanea sativa*, which grows abundantly throughout southern France, Italy, Corsica, and Yugoslavia. Tanning tests indicate a strong similarity to the domestic material, although, being sold either as a solid or a powdered (or spray-dried) extract, the acid content is appreciably lower. The French and Italian powdered product gives a very light brownish-yellow-colored skiver, the solid being somewhat deeper. The Corsican extract tends to give a deeper color but still is very good. Samples of the Yugoslavian product (powdered) examined by the writer were definitely brownish and with something of a dirty cast, no doubt reflecting the lack of competition among the producers. Copper content of these European chestnut extracts is still quite variable, ranging up to 400 ppm or more on the dry basis. Increasing use of stainless-steel equipment is bringing this down, and the better grades usually run 50 to 100 ppm.

Sweetened Chestnut. Just as World War II compelled the British tanner to develop a substitute for chestnut, so the French and Italian tanners had to find a substitute for quebracho, which they did by suitably treating chestnut extract with various alkalizing reagents.[15] The color of the leather produced is similar to that given by ordinary chestnut, but the rate of penetration is said to be much increased and comparable with that of the usual bisulfited quebracho. However, the sweetened chestnut seems to plump rather more and to give a somewhat greater weight yield than bisulfited quebracho.[11]

Oak. Oak tannin is derived mainly from the bark of the common oak (*Quercus robur*), the tanbark oak (*Lithocarpus densiflora*), and the chestnut oak (*Quercus prinus*). While some oak tannin (probably mixed) is obtain-able as an extract containing 25 per cent tans, the greater part is probably obtained locally and leached by the tanner. Owing to increased difficulty in getting supplies, the use of this material has fallen off considerably, though it is said to be in fairly extensive use in California. The tannins appear to be a mixture of pyrogallol and catechol, and the extract contains a fair amount of sugars. The color is a deepish yellow-brown, and the leather is moderately firm and well filled. The rate of penetration is moderate to slow. Other sources of oak bark have been investigated.[8, 75] According to Procter,[68] so-called oak-bark extracts often contain myrobalans and quebracho.

Oakwood. Tannin occurs in the wood of various types of oak, and it is more closely similar to chestnut. The chestnut oak (*Quercus prinus*) produces the best extract but is now difficult to obtain. A sample of a Scandinavian spray-dried extract examined by the writer contained 61 per cent tans, 4.3 per cent ash, and 11 per cent total sugars, and gave a strongly positive test for lignosulfonate by both the Procter-Hirst and Appelius-Schmidt tests.

Valonia. Valonia tannin is obtained from the cups and beards of the acorn of the Mediterranean oak (*Quercus aegilops*) and several subspecies, widely occurring in Greece, Turkey, and Palestine; a general description of the various types, etc., has been given by Gerngross.[26] The beard is richer in tannin than the cup. Much of the raw material is imported and leached by the tanner, but a considerable amount is also imported as a powdered extract of about 63 per cent tannin.

Leached valonia solutions are very prone to deposit bloom; this deposition inside the leather contributes to the solidity and weight yield. Unfortunately, the deposition does not so confine itself, and the material therefore has a definite sludging tendency. The factors governing the deposition of bloom were studied by Sourlangas and Anderson.[88] The color on a skiver is a deepish brown-yellow, and the powdered extract, at least, has a gray or dull cast. On sole leather the tendency is toward a greenish cast. The rate of penetration is moderate to slow. While the extract is less likely to deposit bloom, nevertheless it, too, is a sludge former.

Myrobalans. This tannin occurs in the fruit of a tree, *Terminalia chebula*, indigenous to India. The unripe fruit is richest in tannin and commands a premium price. Much of the imports is in the form of the dried "nuts," which are either leached by the tanner or converted into extract. Because of its high acid content,[19, 84, 102] its use, particularly in warm liquors, is limited.[21] The color is a deepish yellow with, to the writer's eye, a greenish cast which can be quite noticeable in the finished leather. The rate of penetration is on the slow side, but 5 to 10 per cent in the blend tends to give a mellow feel and "cheesy" cut. More than this tends to soften the leather, while, as noted,[21] large amounts can be harmful. The leached liquor has a strong tendency to deposit bloom; the powdered extract is free of this tendency but shows rather high insolubles (3 to 4 per cent).

Sumac. Tanners' sumac is the leaves and small twigs of several species of the genus *Rhus*. *Rhus coriaria* is the source of the genuine Sicilian sumac; good samples contain 25 to 27 per cent tannin. According to Procter,[68] it is frequently adulterated with the ground leaves and twigs of various other shrubs, of which *Pistacia lentiscus* appears to be the most common. Procter refers to the work of Lamb and Harrison[42] for microscopic identification. Sumac is unusual in having a high ash content, largely the salts of weak acids, but typically pyrogallol in its high acidity. It is therefore relatively nonastringent, while the buffer effect of the salts makes it the preferred tanning material for bookbindings, which must often withstand acid atmospheres. Sumac tends to give a soft, mellow leather, and it is much used for retanning. Procter[68] speaks of several United States sumacs, particularly *Rhus glabra*, and seems to imply that the greater part of United States usage derived therefrom (1922); the material was lower in tannin and gave a darker color than the Sicilian product possibly due, as he suggests, to carelessness in harvesting. Russell[76] examined a number of domestic sumacs and found that properly prepared leaves of *Rhus copallina* could satisfactorily replace the Sicilian product, provided[77] some way could be found of economically separating the leaves from the twigs. Sievers and Clarke[80] arrive at a similar conclusion.

Miscellaneous. Divi-divi, algarobilla, and tari are the pods of *Caesalpinia coriaria*, *Caesalpinia brevifolia*, and *Caesalpinia digyna*, respectively. All are liable to ferment, are usually rich in tannin (up to 40 per cent), and are used for both heavy and light leathers in small percentages in the blends. Tari is sometimes preferred to sumac as a base for white and pastel colors, because of its freedom from chlorophyll. For further details of these and other less-common materials, Howes[34] should be consulted.

Another domestic material which has promise as a source of tannin is canaigre, obtained from the root of a species of dock, *Rumex hymenosepalus*, which has been extensively studied by Beebe, *et al.*[7]

The barks of Douglas fir[35] and of ponderosa pine[41] have been investigated by Kurth and Hubbard.

Lignosulfonates. When wood is digested, in the manufacture of paper, with the bisulfites of calcium, magnesium, sodium, or ammonium, the lignins are converted into soluble lignosulfonates which, after purification, are capable of combining with hide. These materials are often misnamed "spruce extract" or "sulfite cellulose." Their combination is of a different type from that of the usual vegetable tannins, and the lignosulfonates do not have leathering properties when used alone. It has been shown[66] that tions which will secure this specificity of reaction on different protein substrates. When one considers this fact, along with Saxon and Harris's observation[35] on the role of the "electrostatic barrier across the surface of the insoluble proteins" in protein acid-base binding, one must conclude that little information of value should be expected from a study of the chemical reactivity of the collagenous fibrous surface before and after tannage. From the information reviewed at this point, one can only conclude that the tanning reaction involves some form of a reversible, unstable reaction between the tanning material and the collagen, and that this reaction has not completely covered or masked the natural reactivity of the collagenous substrate.

THE POTENTIAL FUNCTIONALITY OF THE COLLAGEN-TANNIN SYSTEM

Collagen is a three-strand helix with the three polypeptide chains each incorporating at least three different amino acid residues of glycine, hydroxyproline, and proline. Doty[6] has diagrammatically illustrated the fashion in which the glycine permits the bulky proline and hydroxyproline to fit into the three-strand helix. He further indicates the important role which the hydroxyproline has in the stabilization of the collagen molecule by hydrogen bonding. This configuration of the collagen molecule has been indicated in greater detail in Chapter 4 of Volume I of this monograph.

However, collagen is not composed entirely of these three characteristic amino acids. Other nonpolar amino acids such as alanine, the leucines, and valine are present in such amounts that (taken along with glycine and proline) nonpolar residues comprise about half of the residues in the collagen molecule. Next most important in terms of frequency are the acidic and the basic amino acids responsible for the zwitterionic properties of the native collagen. These have been modified somewhat in the liming of the collagen, so that the collagen to be subjected to vegetable tannage has its isoelectric point at approximately pH 4.8, in contrast to the neutral or slightly alkaline pH found to be the isoelectric point of native collagen. Smaller amounts of such amino acids as serine and threonine add alcoholic hydroxy groups to those arising from the hydroxyproline. Collagen is deficient in such amino acids as the sulfur-containing acids and tryptophane; the absence of the cysteine-cystine system indicates the absence in the protein of the stabilizing effect of the disulfide bridging which has been found so significant in the keratinous proteins.

The presence of functional groups within the collagenous molecule, as evidenced by the functional groups found in the amino acids of the hydrolyzate, does not necessarily assure one that these functional groups will react in the collagenous molecule. Thus, Deasy[5] has observed that such relatively small molecules as are used in the detection of C-terminal and N-terminal amino acids do not readily detect such terminal groups. Among possible explanations for the difficulties encountered, she notes that the terminal groups may be masked by other nonamino acid molecules, or that the terminal groups may be inaccessible to the reacting molecule because of steric effects. Little is known of the disposition of the various functional groups in the collagenous molecule or the possible interaction between the collagenous protein and components of the ground substance bathing the fibers. Furthermore, very little is known of the role of beam-house operations, and in particular liming, in making the reactive sites in the collagenous molecular fabric more reactive. Therefore, some caution is necessary in our attempts to understand better the reaction of collagen with tannins by a consideration of the potential reactive sites in the collagen.

It is possible, however, to summarize the contribution of collagen to tannage, as White[41] has done:

"1. The peptide groups of the helical backbone are available for hydrogen bonding.

"2. Hydroxyl groups from the side chains of hydroxyproline, serine, threonine and tyrosine are available for donor or acceptor hydrogen bonding.

"3. Amino groups are available from the arginine, lysine and histidine residues for donor or acceptor hydrogen bonding as well as the electrostatic salt linkage resulting from the charged NH_3^+ form.

"4. Carboxy groups are available from aspartic and glutamic acid residues for donor or acceptor hydrogen bonding and for the electrostatic salt linkage in the charged COO^- form. It might be noted that native collagen contains a greater or lesser number of these carboxy groups in the amide form, resulting from the presence of asparagine and glutamine in native collagen, and that liming results in a more or less complete removal of ammonia from these amide groups, thereby forming the free carboxy groups.

"5. Polarizable portions of the collagen structure can permit London and van der Waals forces (including dipoles) to contribute to collagen-tannin interaction."

It is also pertinent to note that vegetable tannage is normally carried out on the acid side of the isoelectric point of the limed collagen. The amino groups would be expected to exist in the charged $—NH_3^+$ form, and the carboxy groups will become increasingly discharged, or exist as the unionized $—COOH$ form, as the pH of tannage becomes more acidic.

The complexity of the tanning extracts makes it difficult to state their functionality; this is particularly true since the total composition of the extracts may not contribute to tannin functionality. Thus, only the nontannins might possess a given functional potential. However, one may note that the hydrolyzable tanning extracts certainly possess carboxy groups as well as the alcoholic hydroxy group of the sugars in the extracts. Pyran ether oxygen is found in the vegetable tannins. The characteristic functional group of the vegetable tannins, however, seems to be the phenolic hydroxy group, and yet all phenolic substances are not tanning materials, as is witnessed by the large number of natural and synthetic phenolics which have been found to be incapable of tannage. The interesting work of Russell and his associates[34] on the ability of gallic acid-hexose esters to tan is particularly interesting in this regard. They found that simple esters of gallic acid do not tan, while polyesters of gallic acid and polyhydric alcohol have some tanning abilities, and that certain hexose polygallates are tanning materials equivalent to natural gallotannin. Particularly intriguing is their observation[34c] that fructose pentagallate does not tan, but that glucose pentagallate does. This observation should be checked for its possible significance to the mechanism of the reaction of this type of natural tannins with collagen.

While additional study of the organic chemistry of the natural vegetable tannins may disclose additional functional groups, one might summarize the contribution of the tannins to the collagen-tannin interaction as:

(1) Certain of the tannins possess carboxy groups which, at the pH of tannage, would exist in part in the unionized form, since they are fairly weak acids.

(2) The phenolic hydroxyl groups are the characteristic functional groups in the vegetable tannins, and this group would be expected to be in the un-ionized phenolic form at the pH of tannage.

(3) All of the known functional groups in the vegetable tannins are capable of participating in hydrogen-bonding reactions, as well as interacting by London or van der Waals forces.

POSSIBLE MECHANISMS OF VEGETABLE TANNAGE

The simplest of all possible mechanisms for vegetable tannage would be that which assumes that mere physical deposition of the tannin on the collagenous fibers occurs. It has been noted that this suggestion was made by Knapp[20] a century ago, and through the years it has been offered as a sufficient mechanism for vegetable tannage, chiefly on the basis of the fact that the uptake of the tanning material followed nonstoichiometric patterns which suggested physical adsorptive phenomena. However, our discussion of the stoichiometry of tannin uptake has indicated that such results do not show that purely physical adsorptive forces are involved. The data secured by Lollar and his associates[23] on the uptake of several tannins by calfskin squares, using the pressing technique to minimize the deposition of tannin resulting from spent solution evaporation, have shown that the Langmuir adsorption isotherm, which assumes the presence of specific reactive sites on the adsorbent surface, is sufficient to explain the stoichiometry of the uptake of the tannin. Therefore, our problem becomes not one of defending the absence of reaction, but one of defining the nature of the specific reactive sites.

The foregoing does not imply that mere physical deposition of tanning-material components onto the hide fibers does not contribute to the properties of the commercial leathers produced. The availability of collagenous reactive sites to components of the tanning infusions is too low to make it logical to assume that the total of the large level of material deposited in conventional vegetable tannages is actually reacted with the protein. The observation of White, Kirby, and Knowles[43] that certain tanning-material components enter into solution only because of mutual solubilization, or peptization, furnishes an additional mechanism which would contribute to the deposition of tanning material onto the surfaces of the collagenous fiber without interaction with the protein functionality. The suggestion of White[41] that physical factors in the deposition of tannin deserve far more study than they have had up to the present time is certainly worthy of emphasis.

It has already been noted that the hydrolyzable tannins produce a collagen-tanning-material product which is less stable hydrolytically than the similar product from condensed tannins when such factors as perspiration resistance, digestion by proteolytic enzymes, and resistance to detannage are considered. These observations suggest that the reactions between the tannins and the protein which would require functionality unique to the hydrolyzable tannins are not the characteristic reactions responsible for the phenomenon of vegetable tannage. Thus, it is improbable that the electrostatic saltlike reaction between tanning-material carboxy groups and protein-amino groups are responsible for vegetable tannage. Similarly, one would not conclude that the carbohydrate components of the hydrolyzable tanning materials contribute materially to the mechanism of vegetable tannage. It seems probable that the role of such tanning materials in the customary tanning blends has been more concerned with the physical-chemical control of the tanning process rather than with the essential mechanism of the vegetable tanning reaction. This is further indicated by the observations that proper control of the acid-salt effect in vegetable tannage can permit the use of the single tanning material, wattle, in the production of commercially acceptable vegetable-tanned leather. Thus, Shuttleworth[37] notes that the Leather Industries Research Institute "Osmotan" process, employing 100 per cent wattle, "has been tried out on the large scale by eight tanneries with excellent results, and in several tanneries has been in constant use for nearly two years." The sole leather is noted to be of high grade, with good plumpness, firmness, and yield. Practical experience therefore indicates that the essential characteristics of vegetable tannage can be found solely within the chemical functionality of the condensed tannins.

White[12] has very recently noted that "so far structures have been assigned to only minor non-tannin components of condensed tannin extracts, and no individual tannin has yet been isolated in sufficiently pure condition for determination of its structure." Furthermore, King and White[19] have offered evidence that commercial quebracho extracts contain products of the oxidation and condensation of the native tannins, and that, in the species of trees concerned in the production of this extract, gallotannins appear to be precursors of the condensed tannins. Therefore, we cannot hope at present to postulate specific mechanisms for the reaction of such complex extracts in contact with collagen. Hence, we must still reason from indirect evidence when we attempt to postulate the specific mechanism or mechanisms for tannage with condensed tanning materials. However, the limitation of the significant mechanism of vegetable tannage to that resulting from the chemistry of the condensed tannins does assure us that we are concerned either with a hydrogen-bonding phenomenon or with reactive forces of the London or van der Waals type. Our further understanding of the mechanism requires us to identify the functional group in the protein concerned in the reaction and to evaluate the relative role of these two types of reactive mechanism that seem to be most probable from our knowledge of the condensed tannins.

It seems very probable that the peptide linkage of the protein plays a significant role in the mechanism of vegetable tannage. This is a very old and honored concept in tanning chemistry. Stiasny suggested in 1931[19] that tannin phenolic hydroxy groups coordinate with the peptide carbonyl oxygen group in a bond which has now become known as the hydrogen bond. Grassman, Chu, and Schelz[7] observed that urea-formaldehyde condensates can be used as water-soluble precipitants for the vegetable tannins in the analytical determination of small quantities of the tanning materials. The peptide links in these condensates furnish the only reactive center in the condensate, thus suggesting indirectly that the tannage reaction with the collagenous fabric involves similar reactive groups. Further evidence of this type is found in the observations by Batzer *et al.*[4] that polyamides whose functionality also contains only the peptide link are able to bind vegetable tannins. This concept has also been strengthened by the work of Gustavson; in particular, his paper published in 1954[10] contains the conclusion that "the results indicate the keto-imide groups to be the main and the phenolic groups to be the reactive sites of these tannins." Gustavson[14] also cites the ability of polyvinylpyrrolidone to precipitate tannins as further evidence for the peptide linkage of collagen as the significant reactive site in tannage.

There is ample indirect evidence which suggests the participation of the peptide link in collagen as a site for reaction during vegetable tanning. Its direct demonstration will have to await further research. It is possible that evidence of this type will be secured when single components known to be tanning materials have been isolated from the complex natural tannins. Then their reaction with polymerized nonpolar amino acids, such as polyglycine, would furnish direct evidence that components of the vegetable tanning material complex can react with the peptide link. Monolayer techniques on a surface-tension balance might be a valuable way to secure this needed evidence. Until such evidence is available, one must be content with the conclusion that the indirect evidence strongly suggests that the peptide link is a significant reactive site in the protein fabric.

The conclusion that the peptide link is a significant reactive site in the vegetable tannage of collagen does not imply that the reaction is limited solely to a single reaction site. In the first place, the concept of multipoint fixation of the tanning materials to the protein is now rather generally accepted for many tanning materials, including vegetable tannage. This multipoint fixation could either be one which would involve the peptide links at all fixation points, or it could be one which would involve some other protein functional group in addition to the peptide fixation for one or more of the multipoint-fixation points. The basic amino groups of the protein, in either their charged or their discharged form, have often been suggested as probable reactive sites. The charged amino groups would be particularly expected to react with oppositely charged carboxy groups from the tannin, but we have noted that these probably occur only in the hydrolyzable tanning material which are not typical tannins. Furthermore, the charged amino reactivity of the collagen should be emphasized in such lower-grade tanning materials as the lignosulfonates and the phenolic syntans or quebracho extract that have been subjected to high levels of sulfonation to produce water solubility. These observations suggest that the ability of the charged amino group to react with vegetable tannins is a minor factor in the essential mechanism of vegetable tannage. This is particularly true if one considers the salt-formation reaction between protein amino groups and the tanning material. However, it cannot be concluded that protein amino groups do not react with the tannins, and it must be remembered that these groups could also participate in hydrogen-bonding reactions with the tanning material. Furthermore, one cannot rule out the possibility that the hydroxy groups of the amino acid residues similarly participate in hydrogen-bonding reactions with the tanning materials. It seems rather improbable, however, that the formation of ester or amide linkages between the protein hydroxy or amino groups and the tanning materials is a significant factor in the mechanism of tannage.

This analysis of the probable reaction mechanisms of the vegetable tannins and the protein has left us with only two significant mechanisms. These are the hydrogen bonding of the tannin to the protein through the phenolic hydroxy group of the tanning material, or the binding of the tanning material to the protein through the more diffuse, electrostatic bonds due to forces commonly known as van der Waals forces. Evidence is available to support the role of both types of bonds in vegetable tannage.

Since the structure of the characteristic vegetable tannins is unknown, it is necessary to resort to reaction affinities for analogous compounds with collagen. Tu and Lollar[40] synthesized a group of phenolic substances and explained their varying ability to produce leather (by the use of the solvent tannage system) to their varying probability of hydrogen bonding with the protein. They found that all phenolic hydroxy groups in a xanthene or triphenyl methane compound did not possess equal ability to contribute tanning properties to the compound, but that those phenolic hydroxy groups most likely to participate in hydrogen bonding did contribute to tannage. Furthermore, work on the synthesis of synthetic tannins has customarily led to similar disposition of the phenolic hydroxy groups in the molecule of the synthetic. However, in these latter cases it may only be an accident of the fact that disposition of the phenolic hydroxy groups that is conducive to tannage is also readily formed by synthesis. Insufficient evidence is available to generalize Tu and Lollar's conclusions to more complex phenolic condensates. The very interesting work of Hough[17] on the interaction between boric acid and polynuclear phenolic condensates and the effect of this interaction on the tanning ability of the resultant product is illustrative of the types of reactions which should be studied further. The observations of Tu and Lollar are only indicative of the possibility of hydrogen bonding as the significant reaction in vegetable tannage, and they must remain as such until specific components have been isolated from the vegetable tanning materials, their structure determined, and their ability as tannins evaluated individually. Then, it will be possible to determine the applicability of these ideas to the natural tannins.

Küntzel and Swank[21] have placed more emphasis on the role of secondary valency forces or weak dipoles which result from the aromatic resonance characteristic of the phenolic molecules than they have on the specific effect of hydrogen bonding. Gustavson[15] has reviewed this concept, while Otto[27] has also considered such interpretations of the reaction of aromatic substances with proteins, more particularly with respect to dyeing than to tanning. Otto's conclusion may particularly be given in this regard:[28]

"The conclusion is reached that the simplest type of bond, the type that is the basis for all interactions, is an attraction between dipoles. The peptide bond has a dual nature. In aromatic nuclei, on the other hand, dipoles of corresponding field strength can easily be induced.

"In addition to these generally occurring dipole bonds, hydrogen bridges are also often formed. Both these types of co-ordinate bonds are strongly influenced—often reinforced, but also often weakened—by electrovalencies present.

"The action of these forces between compounds with different numbers of aromatic nuclei on the one hand, and the protein fiber on the other, results in several, widely varying, industrially important effects: the uptake of non-swelling, but at the same time hydrotropically acting, sulphonic acids; tannage with synthetic and vegetable tannins; dyeing with superficially absorbed, or penetrating dyestuffs."

It cannot be denied that both hydrogen bonding and dipole bonds can and do contribute to the interaction between aromatic substances and proteins, but this admission still does not indicate the sufficient condition for the unique phenomenon known as tannage. The positive answer to this question must await further work, and in particular the isolation and identification of single components of a tanning material which do and which do not tan, or produce leather from collagen. Then it will be possible to deduce the sufficient mechanism.

In the meantime, it is the author's conclusion that the most logical mechanism for vegetable tannage is the formation of a hydrogen bond between the aromatic tannin and the protein. In this conclusion he is in agreement with Shuttleworth,[36, 37] Shuttleworth and Cunningham,[38] and White.[41] The latter has said: "The primary fixation, however, is clearly by co-ordinate or H bonding involving both the hydrogen and the oxygen of the phenolic hydroxyl. . . ." This conclusion seems logical to the author of this chapter because:

(1) It is consistent with the stoichiometry of the uptake of the tanning materials by collagen and the ready reversibility of this uptake.

(2) It is consistent with chemical properties of the collagen and the chemical properties of the tanning materials as we know them. In this regard, the author would like to cite the observation of Gustavson of the unique role which hydrogen bonding plays in the stabilization of collagen to the shrinkage-temperature phenomenon.[11] Whether the hydrogen bonding of the tannin to the protein at multipoint fixation spots in the same or adjacent helices is of course unknown for the tannin-collagen complex, but the observed increase in the shrinkage temperature of collagen as a result of tannage would be but a logical extension of the role of the hydroxyproline hydrogen bonds in the stabilization of collagen.

(3) It is consistent with observation that urea solutions, capable of

breaking hydrogen bonds, are able to increase markedly the fixation of vegetable tannins by collagen[8] as well as to detan vegetable-tanned leather, as was noted earlier in our consideration of perspiration deterioration of the leather.

(4) Finally, this reaction mechanism could account for the ability of the collagenous surface to react with large and nonstoichiometric amounts of certain natural tannins and of various synthetic phenolic compounds to produce leather, while other apparently similar phenolics do not possess the tanning ability despite their ability to react with, or color, the collagenous fibrous matrix.

The author would also like to emphasize that it seems probable that the portion of the fixation of the tanning materials by the protein which is responsible for the chemical stabilization of the collagen in tanning may be a relatively small portion of the total amount of tannin deposited on the protein fabric during commercial tannage. The observations of White[41] are quite significant, and the physically deposited tannin found between the tanned fibers may have much to do with the physical and commercial properties of the leather. In this regard the observations of Balfe,[3] cited in Chapter 15 of this volume, should be recalled. Balfe's "tannin deposited on tannin" which occupies the fine capillaries of the hide, although outside of the range of the bonding forces of the collagen, is nevertheless important in establishing the physical characteristics of the leather.

SUMMARY

Our present knowledge of the chemistry of the hide collagen and the vegetable tanning materials is just beginning to attain the status where it can be interpreted intelligently with respect to the mechanism of the reaction between the collagen and the tannins. Since the available information indicates that it is the condensed tannins which are responsible for the characteristic phenomena of tannage, and since our knowledge of the chemistry of the tannins in this class is still very incomplete, it is not possible to state a positive mechanism for the reaction which takes place during vegetable tannage. It seems probable, however, that the characteristic reaction in vegetable tanning involves multipoint hydrogen bonding of the phenolic tannin to the peptide linkage of the collagen. However, it is probable that this factor accounts for a relatively small portion of the total deposited tannin found in commercial leathers. This nonspecific deposition of tanning material in the interstices of the collagenous fabric contributes materially to the commercial properties of the leather, even though it does not play a role in the chemical stabilization, or bonding, of the protein.

Finally, the author would like to suggest consideration of the fact that the current development of the use of organic solvents in practical tanning processes may open up entirely new concepts of the types of materials that can be used to give leathery character of the kind now secured by vegetable tannage. It may well be that vegetable tannage will be replaced largely by tannage of collagen by organic substances, either synthetic or natural, which can be used in solvent tannage systems to produce a wide variety of commercially useful leathers. If that change does occur, and certain pilot-scale developments today suggest that it may, the chapter on solvent tannage systems which will be included in Volume 3 of this series may well foretell the chemist's ultimate mastery of the oldest of man's many chemical processes.

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APPENDIX 1-B

RAW MATERIAL AND WASTE DATA

SLUDGE ANALYSIS

ANALYTICAL RESULTS

MOENCH TANNING COMPANY

Report Date: 9/16/82
Date Received: 8/18/82

PARAMETER	UNITS OF MEASURE	SAMPLE IDENTIFICATION (DATE)
		VACUUM FILTER SLUDGE (8/18/82)
pH	Standard Units	11.60
Dry Weight	%	23
Halogenated Organic Scan	µg/g dry as Chlorine; Lindane Standard	12

COMMENTS: Halogenated organic scan results are used for screening purposes only and are not designed for qualification or quantification of any specific organic compound. Results are calculated based upon the response factor and chlorine content of Lindane, but do not imply either the presence or absence of Lindane itself. Halogenated Organic scan results do not include volatile organic constituents.

Results of the analyses of soils are generally corrected for moisture content and reported on a dry weight basis.

FOR RECRA ENVIRONMENTAL LABORATORIES Deborah J. Praus

DATE 9/16/82

RECRA ENVIRONMENTAL LABORATORIES
I.D. #82-827

ANALYTICAL RESULTS

MONECH TANNING COMPANY
GAS CHROMATOGRAPHY/MASS SPECTROMETRY
PRIORITY POLLUTANT ANALYSES

Report Date: 9/16/82
Date Received: 8/18/82

VOLATILES

COMPOUND	UNITS OF MEASURE	SAMPLE IDENTIFICATION (DATE)
		VACUUM FILTER SLUDGE (8/18/82)
acrolein	µg/kg dry	<1,000
acrylonitrile	µg/kg dry	<1,000
benzene	µg/kg dry	≤25
bromodichloromethane	µg/kg dry	<25
bromoform	µg/kg dry	<25
bromomethane	µg/kg dry	<25
carbon tetrachloride	µg/kg dry	<25
chlorobenzene	µg/kg dry	<25
chloroethane	µg/kg dry	<25
2-chloroethylvinyl ether	µg/kg dry	<25
chloroform	µg/kg dry	<25
chloromethane	µg/kg dry	<25
dibromochloromethane	µg/kg dry	<25
1,1-dichloroethane	µg/kg dry	<25
1,2-dichloroethane	µg/kg dry	<25
1,1-dichloroethylene	µg/kg dry	<25
trans-1,2-dichloroethylene	µg/kg dry	<25
1,2-dichloropropane	µg/kg dry	<25
cis-1,3-dichloropropene	µg/kg dry	<25
trans-1,3-dichloropropene	µg/kg dry	<25
ethylbenzene	µg/kg dry	<25
methylene chloride	µg/kg dry	540

(Continued)

ANALYTICAL RESULTS

MOENCH TANNING COMPANY
GAS CHROMATOGRAPHY/MASS SPECTROMETRY
PRIORITY POLLUTANT ANALYSES

Report Date: 9/16/82
Date Received: 8/18/82

VOLATILES

COMPOUND	UNITS OF MEASURE	SAMPLE IDENTIFICATION (DATE)
		VACUUM FILTER SLUDGE (8/18/82)
1,1,2,2-tetrachloroethane	µg/kg dry	<25
tetrachloroethylene	µg/kg dry	<25
toluene	µg/kg dry	13,000
1,1,1-trichloroethane	µg/kg dry	<25
1,1,2-trichloroethane	µg/kg dry	<25
trichloroethylene	µg/kg dry	<25
trichlorofluoromethane	µg/kg dry	<25
vinyl chloride	µg/kg dry	<25

COMMENTS: Values reported as "less than" (<) indicate the working detection limit for the given sample and/or parameter. Values reported as "less than or equal to" (≤) indicate the presence of a compound at a level below the working detection limit and, therefore, not subject to accurate quantification. Volatiles were analyzed by EPA methodologies ("Determination of Purgeable Organics in Sediment").

FOR RECRA ENVIRONMENTAL LABORATORIES Timothy R Baker

DATE 9/16/82

RECRA ENVIRONMENTAL LABORATORIES
I.D. #82-827

7-30-79

MOENCH TANNING CO.

PROCESS CHEMICALS.

OPERATION	EFFLUENT, gpd.(1)	CHEMICALS
1. WASH MILLS	95,000	None
2. FLESHING	30,000(2)	None
2A. GREASE RENDERING		Sulfuric Acid
3. SOAK	40,000	Bactericide Lime Sodium Sulfhydrate Sodium Sulfide
4. LIMING	60,000	Lime Sodium Carbonate Sodium Sulfhydrate Sodium Sulfide
5. UNHAIRING	30,000	None
5A. HAIR WASHER	65,000	None
6. TAN	40,000	Ammonium Sulfate Non-Ionic Detergent Pancreatic Bate on Wood Flour Beta Naphthol Fungicide Calcium Formate Sodium Chloride Sulfuric Acid Basic Chromium Sulfate Sodium Bicarbonate
7. COLOR MILLS	100,000	Acids - Acetic, Formic, Oxalic Basic Chromium Sulfate Basic Zirconium Sulfate Ammonium Bicarbonate Sodium Bicarbonate Natural Tannins Phenolic Exchange Tannins Naphthalene Syntans - Acid, Neutral

---

(1) To disposal plant unless otherwise indicated.
(2) Combined effluent for fleshing and grease rendering.

OPERATION	EFFLUENT, gpd.	CHEMICALS
7. COLOR MILLS CON'T.		Dyes - Acid, Direct, Chrome, Mettallized, Basic Oils and Waxes - Raw, Sulfated, Sulfonated, Cationic (Amine) Fillers Pigments Clay Wheat Flour Gums - Natural, Synthetic Dispersing Agents - Non-Ionic, Anionic, Cationic Cationic Dye Fixing Agents Sequestering Agents - EDTA Type Anionic Chrome Complexing Agents Anionic Aminoplast Resins Gelatin Sodium Sulfate Aluminum Sulfate Ammonia
8. PASTING	25,000(3)	Methylcellulose Paste
9. BUFFING	12,000	None
10. OLD FINISH	5,000	
10A. NEW FINISH	10,000	Resins Pigments Waxes Dyes Detergents Nitrocellulose Lacquer Emulsions Urethane Lacquer Emulsions Solvents

---

(3) Discharged direct to Cattaraugus Creek.

PART III

SUBSTANCES OF CONCERN
(Refer to attached TABLE I)

Complete all information for those substances your facility has used, produced, stored, distributed or otherwise disposed of since January 1, 1971. Do not include chemicals used only in analytical laboratory work. Enter the name and code from Table I. If facility uses a substance in any of the Classes A – F which is not specified in the list, enter it as code class plus 99, e.g. B99 with name, usage, etc.

NAME OF SUBSTANCE	CODE	AVERAGE ANNUAL USAGE	AMOUNT NOW ON HAND	(✓) GAL.	(✓) LB.	PURPOSE OF USE (State whether produced, reacted, blended, packaged, distributed, no longer used, etc.)
Toluene	D02	1,200	100	X		Lacquer & Dye Solvent
Xylene	D03	25,000	2,000	X		Lacquer & Dye Solvent
4-Nitro Phenol	F03	1,500	600		X	Added to Leather to Act a a Fungicide.
Dyes & Organic Pigments	F24	193,531	22,700		X	Leather Dying & Finishing
Sodium Dichromate	M05	1,200,000	50,000		X	Leather Tanning
Lead	M07	10,000	800		X	Lead Compounds are Presen in some Pigment Materials used for Finishing Leathe
Zirconium Sulfate	M99	200	100		X	Retanning Leather

If you use chemicals of unknown composition, list trade name or other identification, name of supplier and complete information.

NAME OF SUBSTANCE	AVERAGE ANNUAL USAGE	AMOUNT NOW ON HAND	(✓) GAL.	(✓) LB.	SUPPLIER	PURPOSE OF USE (State whether produced, reacted, blended, packaged, distributed, no longer used, etc.)
Busan 30	1,000	500		X	Buckman Laboratories	Fungicide,
Sludgetrol 600 →	5,000	1,000		X	Dearborn Chemical	Boiler Treatment
Steamate 2001	3,500	1,000		X	Dearborn Chemical	Boiler Treatment

I hereby affirm under penalty of perjury that information provided on this form is true to the best of my knowledge and belief. False statements made herein are punishable as a Class A misdemeanor pursuant to Section 210.45 of the Penal Law.

GNATURE (Owner, Partner, or Officer)

DATE November 18, 1983

AME (Printed or Typed) Robert M. Fetterick

TITLE General Mgr. of Operations

STAHL FINISH

BEATRICE CHEMICAL
DIV. OF BEATRICE FOODS CO.

May 7, 1985

Mr. Henk Duwe
Moench Tanning Co., Inc.
Beech & Palmer Street
Box 389
Gowanda, N.Y. 14070

Dear Mr. Duwe,

Attached is the information on the major constituents contained in Stahl Finish products and their respective usages by Moench Tanning for 1984.

This data was based on 12 months sales records from February, 1984 to January 1985.

This tabulation includes all constituents that contribute to V.O.C. content, as well as other constituents that may sometimes be considered to be hazardous.

Do not hesitate to contact me if any additional information is needed.

Sincerely,

Ronald P. Blanchette

Ronald P. Blanchette
Assistant Manager of Safety &
Environmental Affairs

RPB:ab

cc: J.O.
M.G.
E.F.B.
L.I.

26 Howley Street, P.O. Box 3599, Peabody, Massachusetts 01960 • Tel. (617) 531-0371

MONTREAL, P.Q. WAALWIJK NETHERLANDS LOUGHBOROUGH, ENGLAND PARETS SPAIN
MANAGUA, NICARAGUA MEXICO CITY, MEXICO
RIO de JANEIRO, BRAZIL CAGUA, VENEZUELA SYDNEY, AUSTRALIA

MALCOLM PIRNIE

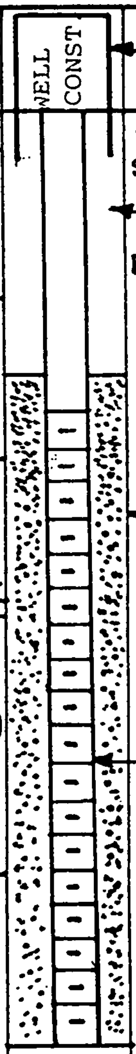
APPENDIX 2-A

BORING LOGS AND MONITORING WELL DETAILS

BORING 1

PROJECT: MOENCH TANNING	PROJECT NO: 605-03-9
DATE: 9-20-83	LOCATION: GOWANDA, N.Y.
DRILLING CONTRACTOR: EARTH DIMENSIONS	INSPECTOR: K. McMANUS
DRILLING METHOD: 3½" HALLOW STEM AUGERS	SAMPLING METHOD: 2-INCH SPLIT SPOON STANDARD PENETRATION TEST
ELEVATION:	DATUM:

SAMPLE no.	SAMPLE depth	blows per 6"		DEPTH	STRATA	SOIL DESCRIPTION density, color, SOIL, admixtures, moisture, other notes, ORIGIN	WELL CONST	REMARKS
S-1	0-2'	3	9			6" TOPSOIL, LEAVES, ROOTS		PROTECTIVE STEEL SLEEVE
		17	17			MEDIUM DENSE, BROWN SAND, WITH SOME SILT & GRAVEL, MOIST & ROOTS, NON PLASTIC		CEMENT BENTONITE SLURRY
S-2	4.5-6.5'	8	13	5		(1" SAND & FINE GRAVEL LENS WITH RED TINT)		
		9	7			MEDIUM DENSE, BROWN, SILT WITH SOME SAND, LITTLE GRAVEL, MOIST NON-PLASTIC		
S-3	9.5-11.5'	1	1	10		(AUGER CHANGE AT 8.5', NO RECOVERY UNTIL 11', POSSIBLE FINE SAND LENS)		
		4	10			MEDIUM DENSE, GRAY, SILT WITH SOME GRAVEL, MOIST, NON-PLASTIC		#4 SAND
S-4	14.5-16.5'	7	17	15		GRADING TO TRACE CLAY, SLIGHTLY PLASTIC		
		19	19			VERY STIFF, GRAY, CLAY, TRACE GRAVEL, MOIST, PLASTIC		
S-5	19.5-21.5'	9	15	20		(OCCASIONAL FINE SAND LENS 1/64")		
		24	26			GRADING TO SILT & CLAY, TRACE GRAVEL, SLIGHTLY PLASTIC.		2-INCH MACHINE SLOTTED PVC WELL SCREEN
S-6	24.5-26.5'	8	32	25		VERY DENSE, GRAY, FINE SAND AND SILT, MOIST, NON PLASTIC		
		41	36					
S-7	29.5-31.5'		4	30		BOTTOM OF BORING AT 29.5'		
		12	13					
				35				



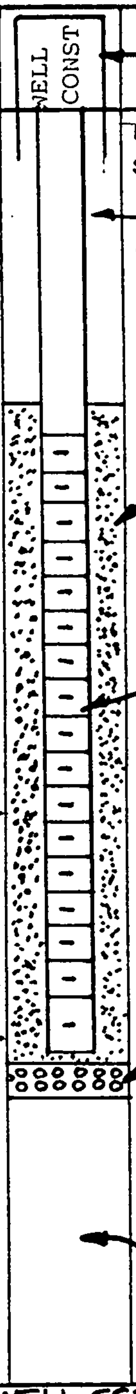
NOTES: MONITORING WELL INSTALLED. 20 FEET OF 2-INCH DIAMETER PVC WELL SCREEN BACKFILLED WITH #4 SAND TO 8 FEET. THERE IS A PROTECTIVE STEEL SLEEVE WITH LOCKING CAP OVER THE STICK-UP.

SHEET 1 OF 1

BORING 2

PROJECT: MOENCH TANNING	PROJECT NO: 605-03-9
DATE: 9-13-83	LOCATION: GOWANDA, N.Y.
DRILLING CONTRACTOR: EARTH DIMENSIONS	INSPECTOR: C. KRAEMER / K. McMANUS
DRILLING METHOD: 3½-INCH HALLOW STEM AUGERS	SAMPLING METHOD: 2-INCH SPLIT SPOON STANDARD PENETRATION TEST
ELEVATION:	DATUM:

SAMPLE no.	SAMPLE depth	blows per 6"		DEPTH	SOIL DESCRIPTION density, color, SOIL, admixtures, moisture, other notes, ORIGIN	REMARKS
S-1	0-2'	3	2		SOFT, GRAY, CLAY AND SILT WITH A TRACE GRAVEL, MOIST PLASTIC	PROTECTIVE STEEL SLEEVE
		2	2			
S-2	2-4'	2	1			
		2	8			
S-3	4-6'	9	14		DENSE, GRAY, SILT, LITTLE GRAVEL MOIST, NON PLASTIC	CEMENT BENTONITE SLURRY
		11	14	5		
S-4	6-8'	6	17			
		17	19			
S-5	8-10'	6	12			
		14	15			
S-6	10-12'	6	10	10	GRADING TO TRACE CLAY, VERY SLIGHTLY PLASTIC	#4 SAND
		14	17			
S-7	12-14'	8	11			
		12	20			
S-8	14-16'	7	13			
		19	23	15		
S-9	16-18'	4	10			
		18	27			
S-10	18-20'	9	20			2-INCH MACHINE SLOTTED PVC WELL SCREEN
		29	36			
S-11	20-22'	6	16	20	GRADING TO HARD, OCCASIONAL SILT TO FINE SAND LENSES (1/64")	
		28	36			
S-12	22-24'	5	8		VERY STIFF, GRAY, CLAY, MOIST PLASTIC	
		12	19			
S-13	24-26'	5	10	25	(OCCASIONAL FINE SAND LENSES 1/64")	
		16	23			
S-14	26-28'	11	14		GRADING TO HARD, TRACE GRAVEL AND SAND	
		44	56			
S-15	28-29.2'	11	53			
		100		30	VERY DENSE, GRAY, FINE SAND & SILT, SOME GRAVEL, MOIST, GLACIAL TILL.	
S-16	30-30.7'	50	100			BENTONITE PELLET SEAL
S-17	32-32.8'	60	100			BACKFILL TO 31.0'
S-18	35-35.3'	100		35		



NOTES: MONITORING WELL INSTALLED. 20' OF 2" DIAMETER PVC WELL SCREEN BACKFILLED WITH #4 SAND TO 8 FEET. THERE IS A PROTECTIVE STEEL SLEEVE WITH LOCKING CAP OVER THE STICK-UP. THE BORING WAS ALLOWED TO BACKFILL UP TO 31 FEET AND A 1 FOOT BENTONITE PLUG WAS INSTALLED TO SEAL THE HOLE AT 30 FEET.

SHEET 1 OF 2

MALCOLM PIRNIE, INC.

BORING 2

PROJECT: MOENCH TANNING
PROJECT NO: 605-03-9
DATE: 9-19-83
LOCATION: GOWANDA, N.Y.
ELEVATION:
DATUM:

SAMPLE				DEPTH	STRATA	SOIL DESCRIPTION density, color, SOIL, admixtures, moisture, other notes, ORIGIN	WELL CONST.	REMARKS
no.	depth	blows per 6"						
S-19	40-42'	38	70			GRADING TO HARD, GRAY, CLAY AND SILT SOME GRAVEL, MOIST GLACIAL TILL		
		64	100					
S-20	45-45.9'	63	100	45				
S-21	50-50.4'	100		50		BOTTOM OF BORING AT 50'		
				55				
				60				
				65				
				70				
				75				
				80				

NOTES:

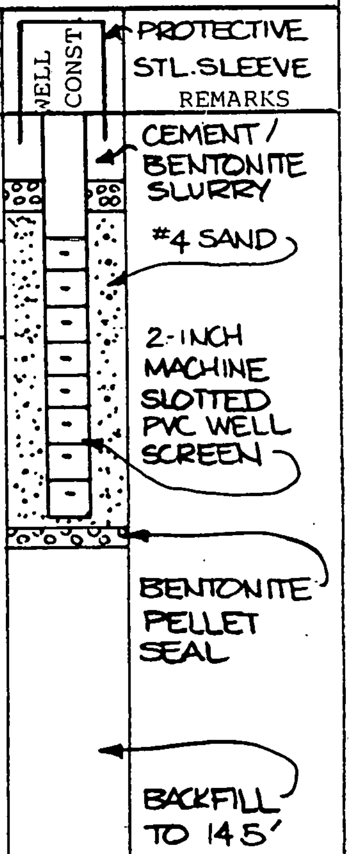
SHEET 2 OF 2

MALCOLM PIRNIE, INC.

BORING 3

PROJECT: MOENCH TANNING	PROJECT NO: 605-03-9
DATE: 9-22-83	LOCATION: GOWANDA, N.Y.
DRILLING CONTRACTOR: EARTH DIMENSIONS	INSPECTOR: K. McMANUS
DRILLING METHOD: 3½-INCH HALLOW STEM AUGERS	SAMPLING METHOD: 2-INCH SPLIT SPOON STANDARD PENETRATION TEST
ELEVATION:	DATUM:

SAMPLE no.	SAMPLE depth	blows per 6"		DEPTH	SOIL DESCRIPTION density, color, SOIL, admixtures, moisture, other notes, ORIGIN
S-1	0-2'	2	12		FILL, BROWN, SILT WITH SOME CLAY, TRACE SAND AND GRAVEL, MOIST. ROOTS THROUGHOUT (6" SAND LENSE AT 1.5')
		20	22		
S-2	4.5-6.5'	4	11	5	VERY STIFF, BLACK CLAY, TRACE SILT, MOIST PLASTIC, SMALL ROOTS GRADING TO GRAY
		16	18		
					VERY DENSE, BLACK, GRAVEL, MOIST GRADING TO VERY DENSE, GRAY, FINE SAND AND SILT, SOME GRAVEL, MOIST, NON PLASTIC, GLACIAL TILL
S-3	9.5-11.5'	27	35	10	
		21	19		
S-4	14.5-14.8'	100		15	
S-5	19.0-19.3'	100			BOTTOM OF BORING AT 19.0'
				20	
				25	
				30	
				35	



NOTES: MONITORING WELL INSTALLED. 10 FEET OF 2-INCH DIAMETER PVC WELL SCREEN BACKFILLED WITH #4 SAND TO 3 FEET. THERE IS A PROTECTIVE STEEL SLEEVE WITH LOCKING CAP OVER THE STICK-UP. THE BORING WAS ALLOWED TO BACKFILL UP TO 14 FEET AND A 6" BENTONITE PLUG WAS INSTALLED TO SEAL THE HOLE AT 13.5 FEET.

SHEET 1 OF 1

MALCOLM PIRNIE, INC.

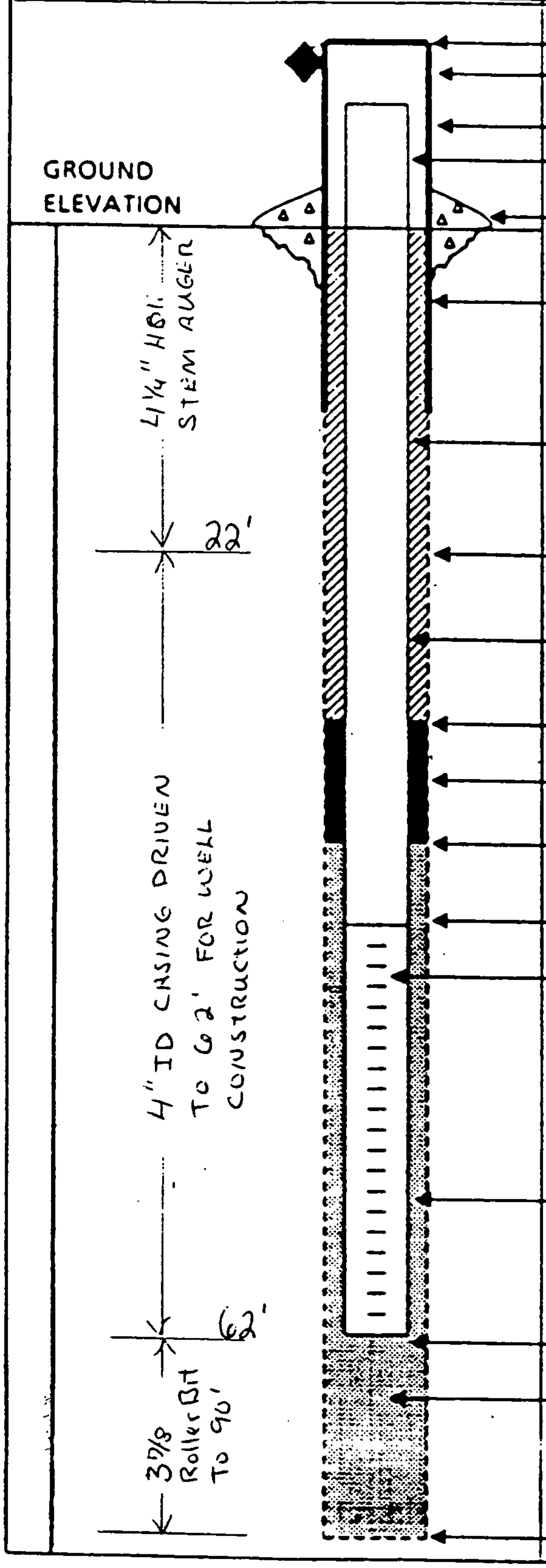
MALCOLM PIRNIE

OVERBURDEN
MONITORING WELL SHEET

PROJECT Palmer St LF
PROJECT NO. 0605-10-1
ELEVATION 804.2 ft.
FIELD GEOLOGIST RHO

LOCATION Gowanda NY
BORING 3D
DATE 8/3/87

DRILLER Buffalo Drilling
DRILLING METHOD 4 1/4" HS / 3 7/8" Auger/Mud Rotar
DEVELOPMENT METHOD Air



ELEVATION OF TOP OF SURFACE CASING: 807.38'
ELEVATION OF TOP OF RISER PIPE: 807.22'
STICK - UP TOP OF SURFACE CASING:
STICK - UP RISER PIPE:
TYPE OF SURFACE SEAL: Cement
I.D. OF SURFACE CASING: 4"
TYPE OF SURFACE CASING: Steel
RISER PIPE I.D. 2"
TYPE OF RISER PIPE: PVC SCH 40
BOREHOLE DIAMETER: 8" to 22' and 4 1/2" to 62'
TYPE OF BACKFILL: Cement/Bentonite Grout
ELEVATION / DEPTH TOP OF SEAL: 757'/47'
TYPE OF SEAL: Bentonite Pellets
DEPTH TOP OF SAND PACK: 753/51'
ELEVATION / DEPTH TOP OF SCREEN: 747.5/56 1/2'
TYPE OF SCREEN: PVC
SLOT SIZE x LENGTH: .010 / 5 Ft
I.D. OF SCREEN: 2"
TYPE OF SAND PACK: #2 Q-ROC
ELEVATION / DEPTH BOTTOM OF SCREEN: 742.5/61 1/2'
ELEVATION / DEPTH BOTTOM OF SAND PACK: 734.5/69 1/2'
TYPE OF BACKFILL BELOW OBSERVATION WELL: Cement Bentonite Grout
ELEVATION / DEPTH OF HOLE: 722/90'

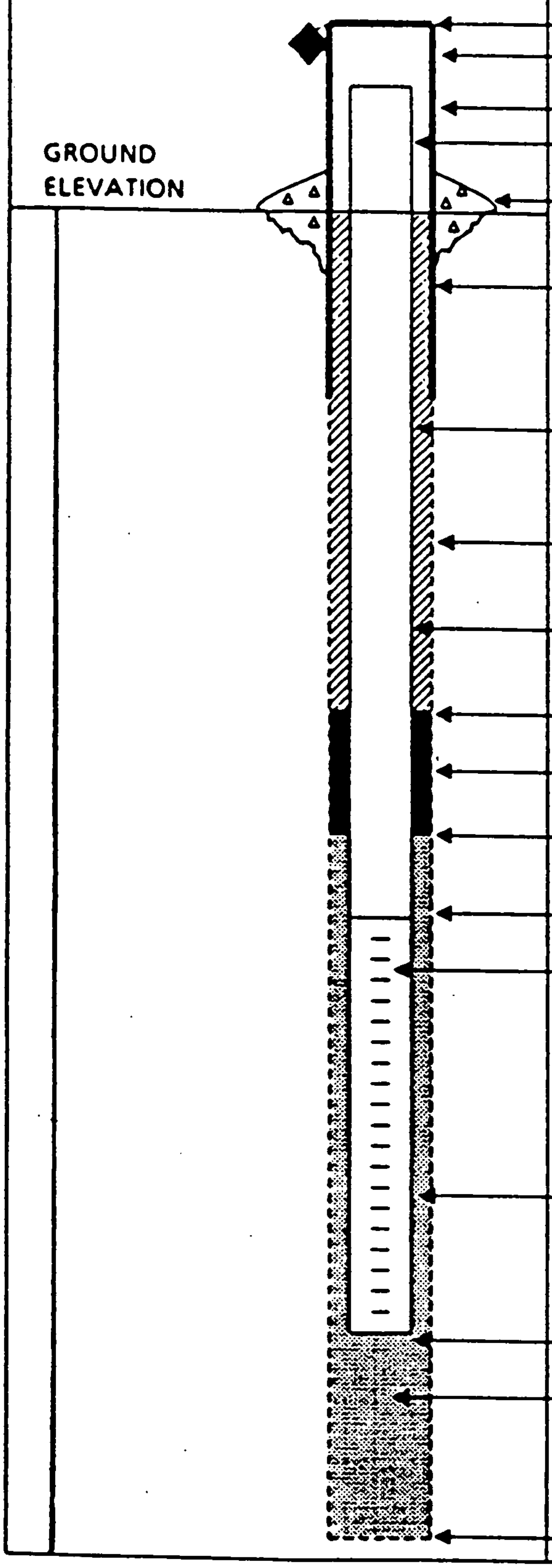
MALCOLM PIRNIE

MONITORING WELL SHEET

PROJECT Moench Tanning Palmer St.
PROJECT NO. 0605-12-1
ELEVATION 804.79
FIELD GEOLOGIST D. Aloysius

LOCATION Gowanda, NY
BORING 3DR
DATE 8/11/88

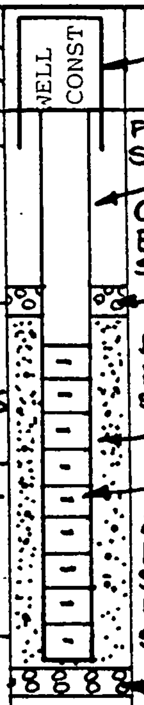
DRILLER Buffalo Drilling
DRILLING METHOD 6" casing to top of rock, then 6" roller bit.
DEVELOPMENT METHOD surge/bail



ELEVATION OF TOP OF SURFACE CASING :
ELEVATION OF TOP OF RISER PIPE:
STICK - UP TOP OF SURFACE CASING:
STICK - UP RISER PIPE : ~2.5ft
TYPE OF SURFACE SEAL: cement/bentonite grout
I.D. OF SURFACE CASING: 4"
TYPE OF SURFACE CASING: steel
RISER PIPE I.D. 2"
TYPE OF RISER PIPE: Sch 40 PVC
BOREHOLE DIAMETER: 10" above 84'; 6" below 84'
TYPE OF BACKFILL: cement/bentonite grout
DEPTH TOP OF SEAL: 82.0'
TYPE OF SEAL: bentonite pellet
DEPTH TOP OF SAND PACK: 86.0'
DEPTH TOP OF SCREEN: 87.0'
TYPE OF SCREEN: Sch 40 PVC
SLOT SIZE x LENGTH: 10 Slot
I.D. OF SCREEN: 2"
TYPE OF SAND PACK: #4 Q-ROK
DEPTH BOTTOM OF SCREEN: 97.0'
DEPTH BOTTOM OF SAND PACK: 100'
TYPE OF BACKFILL BELOW OBSERVATION WELL: #4 Q-ROK Sand
DEPTH OF HOLE: 100'

BORING 4

PROJECT: MOENCH TANNING
PROJECT NO: 605-03-9
DATE: 9-16-83
LOCATION: GOWANDA, N.Y.
DRILLING CONTRACTOR: EARTH DIMENSIONS
INSPECTOR: K. McMANUS
DRILLING METHOD: 3½-INCH HALLOW STEM AUGER
SAMPLING METHOD: 2-INCH SPLIT SPOON STANDARD PENETRATION TEST
ELEVATION:
DATUM:



SAMPLE no.	SAMPLE depth	SAMPLE blows per 6"		DEPTH	SOIL DESCRIPTION density, color, SOIL, admixtures, moisture, other notes, ORIGIN	REMARKS
S-1	0-2'	4	11		FILL, BROWN, LOAMY TOPSOIL	PROTECTIVE STEEL SLEEVE
		11	10		FILL, BLACK, CINDERS	CEMENT/ BENTONITE SLURRY
S-2	5-7'	2	3	5		
		1	11		FILL, YELLOW (PAINT BOOTH SLUDGE), ODOROUS ODOROUS	BENTONITE PELLET SEAL
S-3	10-12'	1	1	10	GRADING TO BROWN, FIBROUS.	#4 SAND
		1	4		FILL, BLACK, CINDERS WITH BRICK FRAGMENTS, ODOROUS (WATER AT 11.5')	2-INCH MACHINE SLOTTED PVC WELL SCREEN
S-4	15-17'	4	10	15		
		9	1		VERY STIFF, GRAY, SILT & CLAY WITH TRACE SAND AND GRAVEL, MOIST, SLIGHTLY PLASTIC	BENTONITE PELLET SEAL
S-5	20-22'	1	4	20		
		6	100		LOOSE, GRAY, SAND WITH SOME GRAVEL AND LITTLE SILT, MOIST NON-PLASTIC	BACKFILL TO 18.5'
S-6	25-26'	6	100	25	GRADING TO VERY DENSE, FINE SAND AND SILT, SOME GRAVEL, MOIST, GLACIAL TILL	
S-7	30-30.95		100	30	BOTTOM OF BORING AT 30'	
				35		

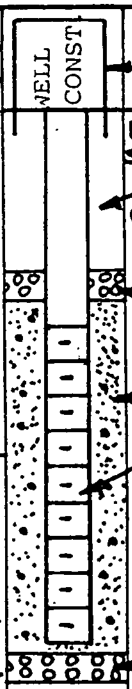
NOTES: MONITORING WELL INSTALLED. 10 FEET OF 2-INCH DIAMETER PVC WELL SCREEN BACKFILLED WITH #4 SAND TO 6.5 FEET. THERE IS A PROTECTIVE STEEL SLEEVE WITH LOCKING CAP OVER THE STICK-UP. THE BORING WAS ALLOWED TO BACKFILL UP TO 18.5 FEET AND A 1 FOOT BENTONITE PLUG WAS INSTALLED TO SEAL THE HOLE AT 17.5 FEET.

SHEET 1 OF 1

BORING 5

PROJECT: MOENCH TANNING	PROJECT NO: 605-03-9
DATE: 9-14-83	LOCATION: GOWANDA, N.Y.
DRILLING CONTRACTOR: EARTH DIMENSIONS	INSPECTOR: C. KRAEMER / K. McMANUS
DRILLING METHOD: 3½-INCH HALLOW STEM AUGERS	SAMPLING METHOD: 2-INCH SPLIT SPOON STANDARD PENETRATION TEST
ELEVATION:	DATUM:

SAMPLE no.	SAMPLE depth	blows per 6"		DEPTH	STRATA	SOIL DESCRIPTION density, color, SOIL, admixtures, moisture, other notes, ORIGIN	REMARKS
S-1	0-2'	9	48			FILL, COBBLES AND GRAVEL WITH SAND AND SOME LEATHER SCRAPS	PROTECTIVE STEEL SLEEVE
		23	29				
							CEMENT/ BENTONITE SLURRY
S-2	4.5-6.5'	5	9			NO RECOVERY, MOSTLY LEATHER SCRAPS	
		6	8	5			
S-3	6.5-8.5'	6	6			NO RECOVERY, MOSTLY LEATHER SCRAPS	BENTONITE PELLET SEAL
		5	6				
S-4	9.5-11.5'	3	6				#4 SAND
		34	36	10			
						VERY DENSE, BROWN, GRAVEL WITH LITTLE SILT AND LITTLE SAND, MOIST, NON PLASTIC (WATER AT 13.5')	2-INCH MACHINE SLOTTED PVC WELL SCREEN
S-5	14.5-16.5'	14	29				
		35	21	15			
						HARD, GRAY, SILT AND CLAY, TRACE GRAVEL, TRACE SAND, MOIST, PLASTIC	BENTONITE PELLET SEAL
S-6	17.5-19.5'	13	26				
		44	74				
S-7	19.5-21.5'	32	74	20			
		70	64			GRADING TO LITTLE GRAVEL & SAND	
						VERY DENSE, GRAY, SAND WITH SOME GRAVEL AND LITTLE SILT, MOIST, NON PLASTIC	BACKFILL TO 18'
S-8	24.5-25.3'	35	100	25			
						GRADING TO FINE SAND & SILT, SOME GRAVEL, MOIST, GLACIAL TILL	
S-9	29.5-30.3'	35	100	30		BOTTOM OF BORING AT 29.5'	
				35			



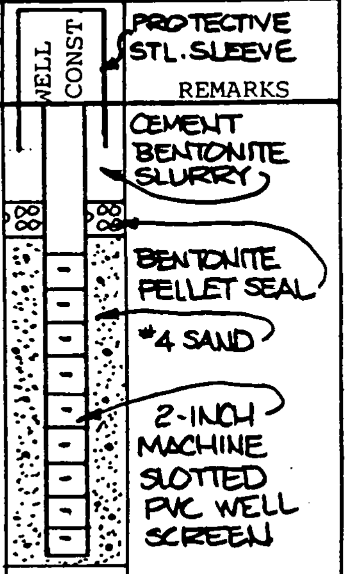
NOTES: MONITORING WELL INSTALLED. 10 FEET OF 2-INCH DIAMETER PVC WELL SCREEN BACKFILLED WITH #4 SAND TO 6 FEET. THERE IS A PROTECTIVE STEEL SLEEVE WITH LOCKING CAP OVER THE STICK-UP. THE BORING WAS ALLOWED TO BACKFILL UP TO 18 FEET AND A 1 FOOT BENTONITE PLUG WAS INSTALLED TO SEAL THE HOLE AT 17 FEET.

SHEET 1 OF 1

BORING 6

PROJECT: MOENCH TANNING
PROJECT NO: 605-03-9
DATE: 9-15-83
LOCATION: GOWANDA, N.Y.
DRILLING CONTRACTOR: EARTH DIMENSIONS
INSPECTOR: K. McMANUS
DRILLING METHOD: 3½"-INCH HALLOW STEM AUGER
SAMPLING METHOD: 2-INCH SPLIT SPOON STANDARD PENETRATION TEST
ELEVATION:
DATUM:

SAMPLE no.	SAMPLE depth	blows per 6"		DEPTH	SOIL DESCRIPTION density, color, SOIL, admixtures, moisture, other notes, ORIGIN
S-1	2-4'	29 17	38 16		FILL, COBBLES AND GRAVEL WITH SAND GRADING TO GRAVEL AND SAND
S-2	4.5-6.5'	3 15	4 23	5	VERY STIFF, BLACK, CLAY WITH SOME SAND AND GRAVEL AND SOME SLAG, MOIST PLASTIC, SOME ROOTS
S-3	9.5-11.5'	3 6	5 9	10	GRADING TO GRAY, CLAY WITH SOME SILT AND GRAVEL, OCCASIONAL COARSE BLACK SAND LENSES (1")
S-4	14.5-14.8'	100		15	REFUSAL AT 14.6'
				20	
				25	
				30	
				35	



NOTES: MONITORING WELL INSTALLED. 10 FEET OF 2-INCH DIAMETER PVC WELL SCREEN WITH #4 SAND TO 4 FEET. THERE IS A PROTECTIVE STEEL SLEEVE WITH LOCKING CAP OVER THE STICK-UP.

SHEET 1 OF 1

MALCOLM PIRNIE, INC.

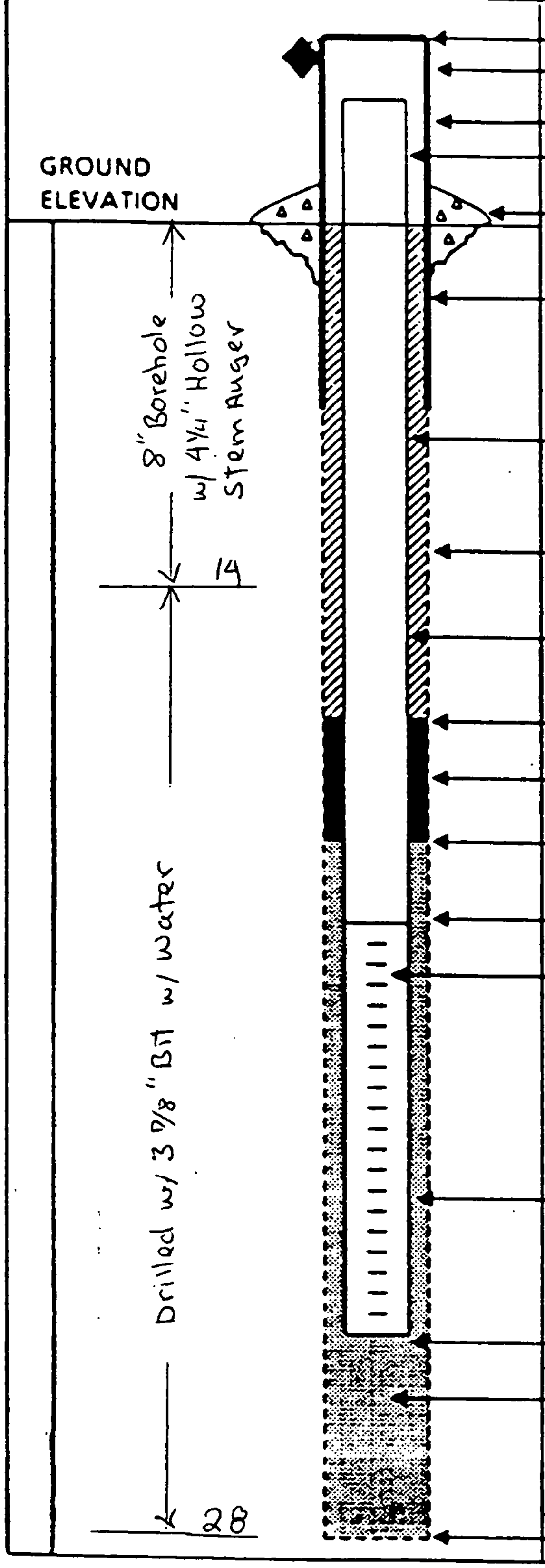
MALCOLM PIRNIE

OVERBURDEN
MONITORING WELL SHEET

PROJECT PALMER ST. LF.
PROJECT NO. 0665-10-1
ELEVATION 795.5ft.
FIELD GEOLOGIST R. O'LASKEY

LOCATION GOWANDA, NY
BORING 7
DATE 8/10/87

DRILLER D. ALTROGGIE
DRILLING METHOD 3 7/8" Rotary Bit 4 1/4" HS. AUGER
DEVELOPMENT METHOD AIR

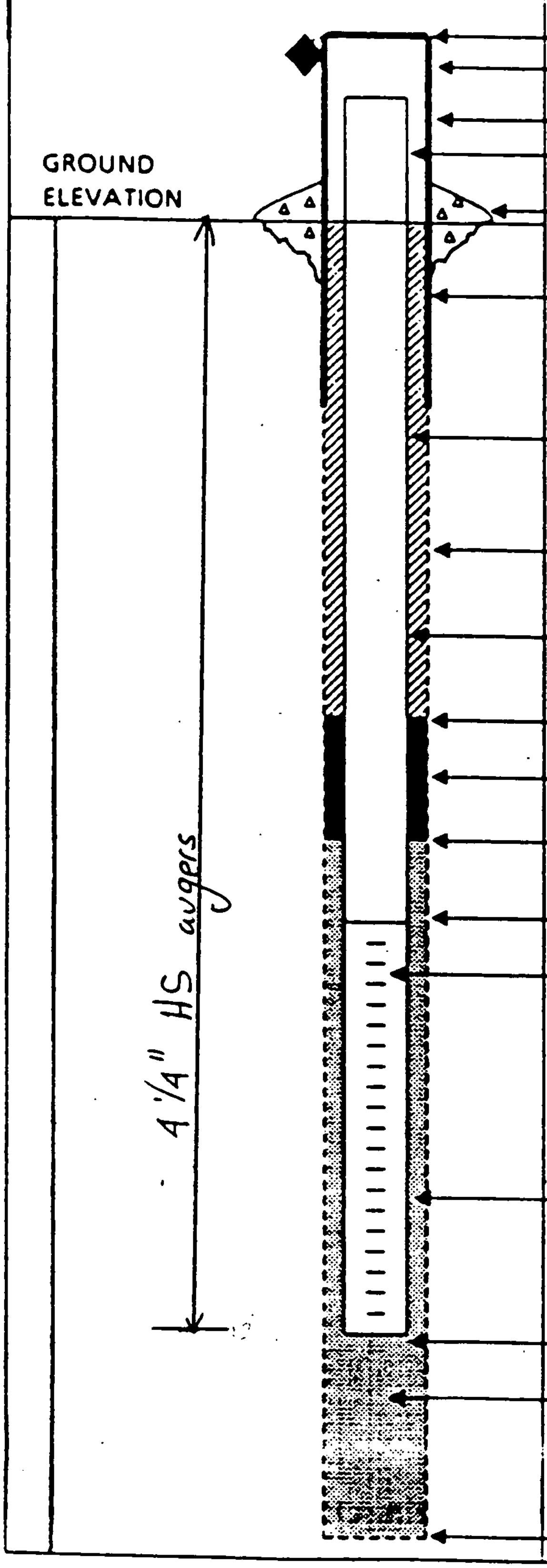


ELEVATION OF TOP OF SURFACE CASING: 800.67'
ELEVATION OF TOP OF RISER PIPE: 800.50'
STICK - UP TOP OF SURFACE CASING:
STICK - UP RISER PIPE:
TYPE OF SURFACE SEAL: CEMENT
I.D. OF SURFACE CASING: 4"
TYPE OF SURFACE CASING: STEEL
RISER PIPE I.D. 2"
TYPE OF RISER PIPE: SCH 40 PVC
BOREHOLE DIAMETER: 8" to 14' and 4" to 28'
TYPE OF BACKFILL: CEMENT / BENTONITE
ELEVATION / DEPTH TOP OF SEAL: 780.5/17'
TYPE OF SEAL: BENTONITE PELLETS
DEPTH TOP OF SAND PACK: 776.8/20.7'
ELEVATION / DEPTH TOP OF SCREEN: 775.0/22.5'
TYPE OF SCREEN: PVC
SLOT SIZE x LENGTH: .010"/5 FT
I.D. OF SCREEN: 2"
TYPE OF SAND PACK: #2 Q-ROC
ELEVATION / DEPTH BOTTOM OF SCREEN: 770.0/27.5'
ELEVATION / DEPTH BOTTOM OF SAND PACK: 769.0/28'
TYPE OF BACKFILL BELOW OBSERVATION WELL: N/A
ELEVATION / DEPTH OF HOLE: 769.0/28'

MALCOLM PIRNIE

OVERBURDEN MONITORING WELL SHEET

PROJECT PALMERST LF.
PROJECT NO. 0605-10-1
ELEVATION 797.5'
FIELD GEOLOGIST R O'LASKEY
LOCATION GOWANDA, NY
BORING 7S
DATE 8/7/87
DRILLER D. ALTROGGIE
DRILLING METHOD 4¼" HS AUGER
DEVELOPMENT METHOD AIR



ELEVATION OF TOP OF SURFACE CASING: 800.54'
ELEVATION OF TOP OF RISER PIPE: 800.38'
STICK - UP TOP OF SURFACE CASING:
STICK - UP RISER PIPE:
TYPE OF SURFACE SEAL: CEMENT
I.D. OF SURFACE CASING: 4"
TYPE OF SURFACE CASING: STEEL
RISER PIPE I.D. 2"
TYPE OF RISER PIPE: SCH 40 PVC
BOREHOLE DIAMETER: 8"
TYPE OF BACKFILL: CEMENT/BENTONITE
ELEVATION / DEPTH TOP OF SEAL: 795./2½'
TYPE OF SEAL: Bentonite/PELLETS
DEPTH TOP OF SAND PACK: 793.0/4½'
ELEVATION / DEPTH TOP OF SCREEN: 790.5/7'
TYPE OF SCREEN: PVC
SLOT SIZE x LENGTH: .010"/ 5 FT
I.D. OF SCREEN: 2"
TYPE OF SAND PACK: #2 Q-ROC
ELEVATION / DEPTH BOTTOM OF SCREEN: 785.5/12'
ELEVATION / DEPTH BOTTOM OF SAND PACK: 784.5/13'
TYPE OF BACKFILL BELOW OBSERVATION WELL: N/A
ELEVATION / DEPTH OF HOLE: 784.5/13'

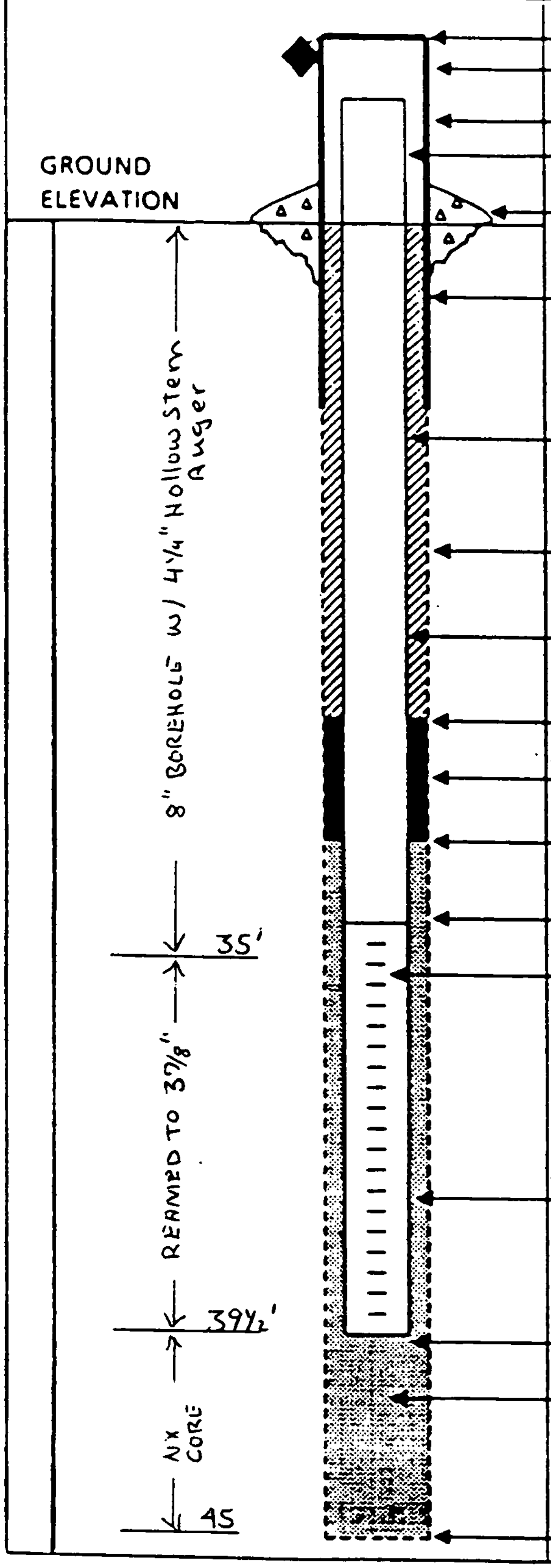
MALCOLM PIRNIE

OVERBURDEN
MONITORING WELL SHEET

PROJECT PALMER ST. LF
PROJECT NO. 0605-10-1
ELEVATION 797.5'
FIELD GEOLOGIST R. O'Laskey

LOCATION GOWANDA, NY
BORING 7D
DATE 8/6/87

DRILLER D. Altroggie
DRILLING METHOD NX CORE 4¼" HS AUGER
DEVELOPMENT METHOD



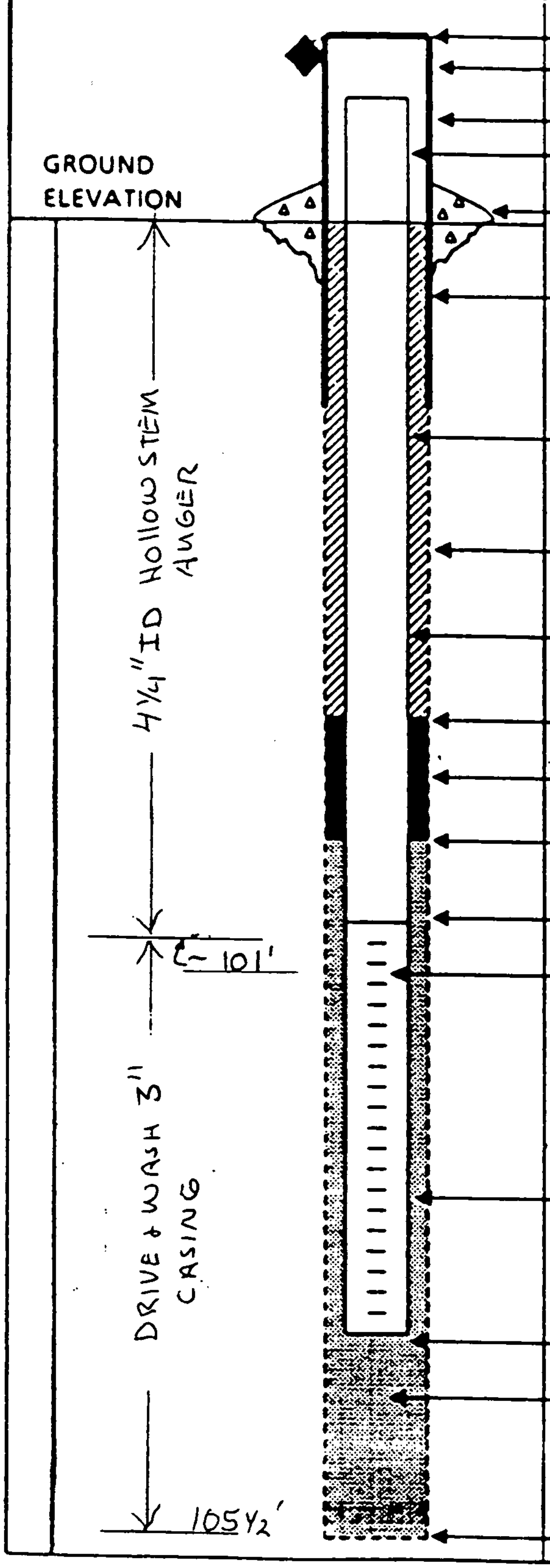
ELEVATION OF TOP OF SURFACE CASING: 800.55'
ELEVATION OF TOP OF RISER PIPE: 800.40'
STICK - UP TOP OF SURFACE CASING:
STICK - UP RISER PIPE :
TYPE OF SURFACE SEAL: CEMENT
I.D. OF SURFACE CASING: 4"
TYPE OF SURFACE CASING: STEEL
RISER PIPE I.D. 2"
TYPE OF RISER PIPE: SCH 40 PVC
BOREHOLE DIAMETER: -8" to 35'
-4" to 39½'
-3" to 45'
TYPE OF BACKFILL: CEMENT/BENTONITE
ELEVATION / DEPTH TOP OF SEAL: 769.5/28'
TYPE OF SEAL: bentonite pellets
DEPTH TOP OF SAND PACK: 765.5/32'
ELEVATION / DEPTH TOP OF SCREEN: 763.5/34'
TYPE OF SCREEN: PVC
SLOT SIZE x LENGTH: 0.010" / 5ft.
I.D. OF SCREEN: 2"
TYPE OF SAND PACK: # 2 Q-ROC
ELEVATION / DEPTH BOTTOM OF SCREEN: 758.5/39'
ELEVATION / DEPTH BOTTOM OF SAND PACK: 39½
TYPE OF BACKFILL BELOW OBSERVATION WELL: Cuttings from Reaming w/ 3⅞" Bit and #2 Q ROC
ELEVATION / DEPTH OF HOLE: 752.5/45'

MALCOLM PIRNIE

OVERBURDEN
MONITORING WELL SHEET

PROJECT PALMER ST. LF.
LOCATION GOWANDA, NY
PROJECT NO. 0605-10-1
BORING 8
ELEVATION 797.5
DATE 8/27/87
FIELD GEOLOGIST R. O'LASKEY

DRILLER D. ALTROGGIE
DRILLING METHOD as below
DEVELOPMENT METHOD AIR



ELEVATION OF TOP OF SURFACE CASING: 818.53
ELEVATION OF TOP OF RISER PIPE: 818.31
STICK - UP TOP OF SURFACE CASING:
STICK - UP RISER PIPE:
TYPE OF SURFACE SEAL: CEMENT
I.D. OF SURFACE CASING: 4"
TYPE OF SURFACE CASING: STEEL
RISER PIPE I.D. 2"
TYPE OF RISER PIPE: SCH 40 PVC
BOREHOLE DIAMETER: 8" to 101'/
TYPE OF BACKFILL: CEMENT/BENTONITE
ELEVATION / DEPTH TOP OF SEAL: 717.5/80'
TYPE OF SEAL: BENTONITE SLURRY
DEPTH TOP OF SAND PACK: 700.5/97'
ELEVATION / DEPTH TOP OF SCREEN: 697.0/100.5'
TYPE OF SCREEN: PVC
SLOT SIZE x LENGTH: .010"/5FT
I.D. OF SCREEN: 2"
TYPE OF SAND PACK: COLLAPSED FORMATION (SAND AND GRAVEL
ELEVATION / DEPTH BOTTOM OF SCREEN: 692.0/105.5'
ELEVATION / DEPTH BOTTOM OF SAND PACK: 692.0/105.5'
TYPE OF BACKFILL BELOW OBSERVATION WELL: Collapsed Sand and Gravel
ELEVATION / DEPTH OF HOLE: 692.0/105.5'

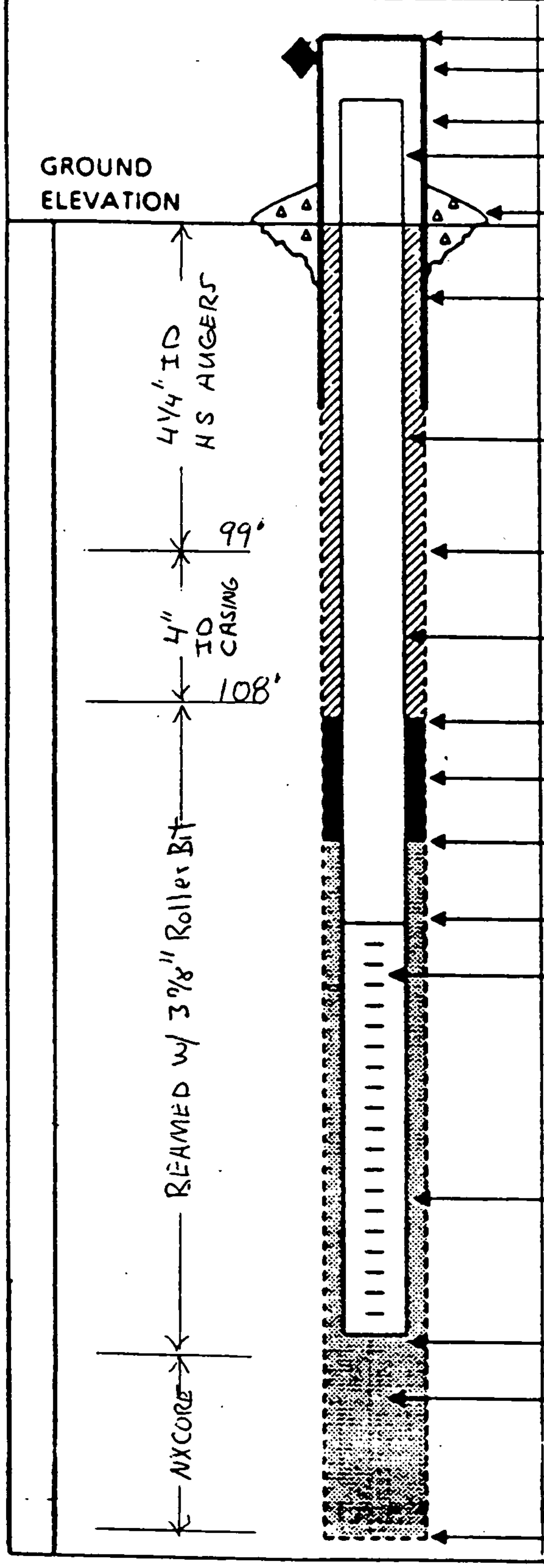
MALCOLM PIRNIE

OVERBURDEN
MONITORING WELL SHEET

PROJECT PALMER ST. LF
PROJECT NO. 0605-10-1
ELEVATION 816.0'
FIELD GEOLOGIST R. O'LASKEY

LOCATION GOWANDA, NY
BORING 8D
DATE 8/21/87

DRILLER D. ALTROGGLE
DRILLING METHOD Hollow Stem Auger Mud Rotary ~~Drive & Wash~~
DEVELOPMENT METHOD AIR



ELEVATION OF TOP OF SURFACE CASING: 818.63'
ELEVATION OF TOP OF RISER PIPE: 818.45'
STICK - UP TOP OF SURFACE CASING:
STICK - UP RISER PIPE:
TYPE OF SURFACE SEAL: CEMENT
I.D. OF SURFACE CASING: 4"
TYPE OF SURFACE CASING: STEEL
RISER PIPE I.D. 2"
TYPE OF RISER PIPE: SCH 40 PVC
BOREHOLE DIAMETER: 4" 108' to 122'
TYPE OF BACKFILL: CEMENT / BENTONITE
ELEVATION / DEPTH TOP OF SEAL: 707.0/109'
TYPE OF SEAL: BENTONITE SLURRY
DEPTH TOP OF SAND PACK: 701.5/114.5'
ELEVATION / DEPTH TOP OF SCREEN: 699.0/117'
TYPE OF SCREEN: PVC
SLOT SIZE x LENGTH: .010" / 5 FT
I.D. OF SCREEN: 2"
TYPE OF SAND PACK: #2 Q-ROC
ELEVATION / DEPTH BOTTOM OF SCREEN: 694.0/122'
ELEVATION / DEPTH BOTTOM OF SAND PACK: 693.0/123'
TYPE OF BACKFILL BELOW OBSERVATION WELL: Cuttings from Reaming w/ 3 7/8" Bit.
ELEVATION / DEPTH OF HOLE: 689.0/127'

MALCOLM PIRNIE

FIELD BOREHOLE LOG
ROCK DRILLING

CLIENT MOENCH TANNING
PROJECT
SITE PALMER STREET LANDFILL
LOCATION GOWANDA, NY
CONTRACTOR BUFFALO DRILLING
METHOD OF BORING: SOIL 6¼" ID AUGER / 6¼" CASING
ROCK NX CORE

JOB NO. 0605-124 HOLE NO. 3RR-1 SHEET NO. 1 OF 4
WEATHER Clear INSPECTOR RHO
TEMP. 80 °F STARTED 12:30 P.M. 7-25 1988
DIP ° FINISHED 4:30 P.M. 8-3 1988
ELEVATIONS: DATUM
CASING DIAM.
GROUND SURFACE
CORE DIAM. WATER LEVELS

LOG	DESCRIPTION: COLOR, TEXTURE, FOLIATION, JOINTING, FRACTURING, ALTERATION, FAULTING, HARDNESS, CEMENTING, ETC.	ELEV. DEPTH	ROCK CORE RUN NO.	ROCK CORE RUN LENGTH	ROCK CORE REC'D	ROCK CORE RQD	NOTES: BORING, TESTING AND SAMPLING PROCEDURES; WATER LOSS AND GAIN; HOLE CAVING; LOST CORE; CEMENTING; ETC.
							DRILL W/ 6¼" ID AUGERS TO 1ST ENCOUNTER WITH VERY HARD DRILLING AT 82 FT.
							TOOK (1) SPLIT SPOON SAMPLE AT 56-58'. OBSERVED A DAMP TILL (f SAND and SILT, tr C sand f Gravel - 100 Blows/5"
							AUGERING FROM 52 TO 62 FT ENCOUNTERED ALTERNATELY HARD AND LESS HARD DRILLING CONDITIONS - UNIFORMLY HARD DRILLING ABOVE 52 FT AND BELOW 62 FT
							BEGAN DRILLING OVERBURDEN AT 12:30 ON 7-25 COMPLETED BOREHOLE IN OVERBURDEN AT 4:30 on 7-27 APPROX 20 hrs/83 FT
							SEAT AUGERS (1) FOOT INTO ROCK AT 83 FT BEGIN CORING 1ST 10 FT AT 2:30 PM 7-28 END 1ST 9 FT AT 4:45 PM
							Ended Run at 92 FT - RAN OUT OF WATER.

MALCOLM PIRNIE

FIELD BOREHOLE LOG
ROCK DRILLING

JOB NO ______ HOLE NO 3DR-1 SHEET NO 2 OF 4

RECOVERY 7.0'/9.0'

RQD 67/84 x100 = 80%

Natural Fractures are ZONES WHERE THE ROCK IS HIGHLY BROKEN-UP INTO ½" to 1" PIECES - TYPICALLY ASSOC w/ M to F SAND ADHERING to THE ROCK FRAGMENTS. AT ONE ZONE (86.7 - 87.0) A CLAYEY SAND IS PRESENT

DRILL BREAKS ARE PLANAR smooth Generally 90° To CORE AXIS - EXCEPT IN 4 ~~to~~ LOCATIONS WHERE 0° or 45° BREAKS OCCURRED

SEVERAL CLOSED CRACKS at 0° to 45° TO CORE AXIS ARE PRESENT -

DRILL BREAK SURFACES TYPICALLY HAVE NO INFILLING OF SAND

CORE HOLE FILLED TO 85 FT BELOW TOP OF AUGER - PROBABLY WITH SAND - VERY SOFT ON BOTTOM OF HOLE - AND SANDY WATER CAME OUT OF CORE BARREL + INFILLED FRACTURES IN CORE

7-29

SAND IS INFERRED TO BE ~~CO~~ ENTERING HOLE FROM BENEATH AUGERS OR THROUGH

MALCOLM PIRNIE

FIELD BOREHOLE LOG
ROCK DRILLING

JOB NO. ______ HOLE NO. 3DR-1 SHEET NO. 3 OF 4

85
+.5
85.5
2.5
83.0

JOINT

AUGER CONNECTIONS - NEED TO BLOCK SAND FLOW

SEAT AUGERS ANOTHER 10" TO 83.8 ft - DRILLERS LV AT 9AM TO GET 3" CASING TO SEAT OVER COREHOLE.

3" CASING WILL ELIMINATE SAND + REDUCE WATER REQUIREMENTS, INCREASE UPHOLE VELOCITY NEEDED TO FLUSH OUT SAND

MONDAY 9AM - PULL AUGERS HOLE STAYS OPEN TO 83 ft NOTED F. Gravel / C. SAND cuttings on AUGER FLIGHTS 70-75' MAY BE FROM ABOVE

LOWER A STRING OF 6" FLUSH CASING - WILL PRODUCE AN ≈6.5 inch hole - LOWER CASING TO 83 FT.

~~A~~ SPIN CASING TO 83.5 ADVANCES VERY SLOWLY

ATTEMPTED TO ROLLER BIT AHEAD OF CASING. CASING FILLED WITH ~~SE~~ SEDIMENT TO 70 FT - ATTEMPT TO DRILL AND FLUSH TO CLEAN-OUT CASING - BUT ~~MAT~~ CASING CONTINUES TO FILL.

REMOVE ROLLER BIT AND CONTINUE TO ADVANCE

MALCOLM PIRNIE

FIELD BOREHOLE LOG
ROCK DRILLING

JOB NO ______ HOLE NO 3DR-1 SHEET NO 4 OF 4

CASING - TOTAL ADVANCE
TO 84 FT - VERY SLOW
THEN ZERO ADVANCE

TAPE HOLE TO 79½
BELOW TOP OF CASING
≙ 27 BELOW GROUND

GO TO ROLLER BIT -
LOWER BIT TO 50 FT
~~BIT~~ (TOC): BIT STOPS

TAPE HOLE TO 77½
BELOW TOC - WEIGHT
ON TAPE BECAME STUCK
AT 77½ FT

LOWER ¾" STEEL PIPE
TO 79½ FT. DISLODGE
TAPE

TUESDAY AM
~~PU~~ PULL CASING
CASING SHEARED
AT TOP OF THREADS
AT 50 FT

WED: AM OBTAIN FISHING
TOOLS AND Abandon Hole
TUES · REMAINDER OF DAY
GO TO DEVELOPMENT OF
EXISTING WELLS

MALCOLM PIRNIE

DRILLING REPORT
(CORE DETAILS)

CLIENT MOENCH TANNING
PROJECT
SITE PALMER STREET LANDFILL

JOB NO. 0605-12-1
HOLE NO. 3DR-4
SHEET NO. 1 OF 2

DEPTH (FT.)	DISCONTINUITY								DESCRIPTION																						MUTUAL ANGLE
	JOINT	FRACTURE	DRILL BREAK	FAULT	BEDDING PL				ANGLE WITH CORE AXIS	TIGHT	PART OPEN	OPEN	REHEALED		SLT. WEATH'D	MOD WEATH'D	HIGH WEATH'D	SLICK	SMOOTH	ROUGH	PLANE	CURVED	IRREGULAR	SLICKENSIDED	FILLING	STAINING	BLEACHING	M/F SAND			
83.0		X										X																X			
1		X										X																X			
2		X										X																X			
3																															
4																															
5																															
6		X										X																			
7		X										X																			
8		X										X																			
9		X										X																			
84.0			X																												
1			X																												
2			X																												
3		X										X																X			
4		X										X																X			
5			X						0°																						
6		X										X																X			
7		X										X																X			
8		X										X																X			
9			X																												
85.0			X																												
1			X																												
2			X																												
3			X																												
4			X																												
5		X										X																X			
6			X																												
7			X																												
8			X																												
9			X																												
86.0			X																												
1			X																												
2			X																												
3			X																												
4			X																												
5			X																												
6			X																												
7			X																												
8		X										X													CL			X			
9		X										X													CL			X			
87.0		X										X													CL			X			
1			X																												
2																															
3			X																												
4																															
5			X																												
6																															
7			X																												
8																															
9			X																												
88.0																															
1			X						0°																						
2																															
3			X																												
4			X																												
5																															
6																															
7			X																												
8			X																												
9			X																												

C = CARBONATE H = HEMATITE K = CHLORITE Q = QUARTZ L = LIMONITE CL = CLAY PY = PYRITE

MALCOLM PIRNIE

DRILLING REPORT
(CORE DETAILS)

CLIENT MOENCH TANNING
PROJECT
SITE PALMER STREET LANDFILL

JOB NO. 0605-12-1
HOLE NO. 3DR-1
SHEET NO. 2 OF 2

DEPTH (FT.)	DISCONTINUITY								DESCRIPTION																							MUTUAL ANGLE
	JOINT	FRACTURE	DRILL BREAK	FAULT	BEDDING PL				ANGLE WITH CORE AXIS	TIGHT	PART OPEN	OPEN	REHEALED		SLT. WEATH'D	MOD. WEATH'D	HIGH WEATH'D	SLICK	SMOOTH	ROUGH	PLANE	CURVED	IRREGULAR	SLICKENSIDED	FILLING	STAINING	BLEACHING					
89.0			X																													
1			x																													
2																																
3			X																													
4																																
5			X																													
6									40°																							
7			X						45°																							
8																																
9			X																													
90.0																																
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2																																
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C= CARBONATE H= HEMATITE K= CHLORITE Q=QUARTZ L=LIMONITE CL=CLAY PY=PYRITE

MALCOLM PIRNIE

FIELD BOREHOLE LOG
ROCK DRILLING

CLIENT Moench Tanning
PROJECT Palmer St / Hydrogeo
SITE Palmer St
LOCATION Gowanda, NY
CONTRACTOR Buffalo Drilling
METHOD OF BORING: SOIL
ROCK NX coring; then 6" roller bit ream.

JOB NO. 0605-12-1 HOLE NO. 3DR-2 SHEET NO. 1 OF 1
WEATHER Sunny INSPECTOR DLA
TEMP. 90 °F STARTED 10^15 A.M. 8/8 19 88
DIP 0 ° FINISHED 3^30 P.M. 8/8 19 88
ELEVATIONS: DATUM
CASING DIAM. 6" to 84' 1' into rock.
CORE DIAM. 2 7/8"
GROUND SURFACE
WATER LEVELS

LOG	DESCRIPTION: COLOR, TEXTURE, FOLIATION, JOINTING, FRACTURING, ALTERATION, FAULTING, HARDNESS, CEMENTING, ETC.	ELEV. / DEPTH	ROCK CORE RUN NO.	RUN LENGTH	REC'D	RQD	NOTES: BORING, TESTING AND SAMPLING PROCEDURES; WATER LOSS AND GAIN; HOLE CAVING; LOST CORE; CEMENTING; ETC.
Shale	Shale: grey/black, very broken; rock is slightly weathered along bedding surfaces. One high angle fracture observed at approx. 90.5' which appeared moderately weathered.	84'	1	9	7.0	% 0	Note: core edges are grooved and pitted which may be caused by drilling? Bedding plane surfaces are fairly smooth. Open bedding planes in the rock may have been filled with clay which washed away during drilling. Most breaks appear to be natural (bedding planes). Core edges, near breaks, show less resistence than other portions of the rock being more pitted and grooved around these particular areas. Refer to Pressure Test data for permeability estimates.
	Same: rock is still very broken but less than 1st run. Trace of clay observed between some breaks. Again, most breaks appear natural exhibiting similar characteristics as above.	93 ↓ 103	2	10	9	7%	↓

APPENDIX 3-A

UNIVERSAL SOIL LOSS EQUATION CALCULATIONS

BY TJR DATE 2/6/89 SHEET NO. 1 OF 3
CHKD. BY KRM DATE 2/8/89 JOB NO. 0605-12-1
SUBJECT Palmer Street Landfill

EVALUATION OF EROSION POTENTIAL FOR SLOPES GREATER THAN 5% AT PALMER STREET LANDFILL

ASSUMPTIONS: FAILURE OF LANDFILL SLOPES WOULD BE DUE TO RAINFALL INDUCED EROSION - NOT TO INTERNAL SHEAR FAILURE OF CLAY SOIL FORMING THE SLOPES.

FROM: USEPA MANUAL
"EVALUATING COVER SYSTEMS FOR SOLID AND HAZARDOUS WASTE"
PP 37-43

EQUATION: $A = RKLSCP$

A = AVERAGE ANNUAL SOIL LOSS, TONS/ACRE
R = RAINFALL + RUNOFF EROSIVITY INDEX
K = SOIL ERODIBILITY FACTOR
L = SLOPE-LENGTH FACTOR
S = SLOPE-STEEPNESS FACTOR
C = COVER-MANAGEMENT FACTOR
P = PRACTICE FACTOR

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BY TJR DATE 2/89 SHEET NO. 2 OF 3

CHKD. BY KRm DATE 2/89 JOB NO. 0605-12-1

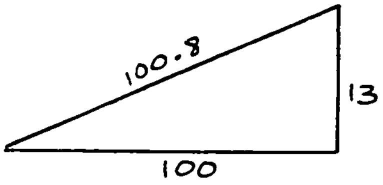
SUBJECT Palmer Street Landfill

R (FROM FIG. 20, PAGE 37 OF MANUAL) = 100

K (TABLE 5, PAGE 38 OF MANUAL FOR CLAY WITH <0.5% ORGANICS) = 0.13

LS FACTOR (TABLE 6, PAGE 39)

- CHECK SLOPE OF AREA 3 AS IT IS THE STEEPEST.
- TYPICAL SLOPE SECTION FROM STEEPEST SIDE



SLOPE LENGTH = 100.8

% SLOPE = $\frac{13}{100}(100) = 13\%$

LS FACTOR = 2.05

C FACTOR (FROM TABLE 7, PAGE 40 MEADOW - GRASS & LEGUME MIX) = 0.01

P FACTOR (FROM TABLE 8, PAGE 41) = 1.0

$A = R K L S C P$

$= (100)(0.13)(2.05)(0.01)(1.0)$

$= 0.27$ TONS/ACRE/YEAR

SINCE THE NYSDEC ALLOWABLE LIMIT FOR EROSION IS 2 TONS/ACRE/YEAR, 13% SLOPES WITH AN EROSION RATE OF 0.27 TONS/ACRE/YEAR ARE ACCEPTABLE. ALL OTHER SLOPES ARE LESS THAN THIS, THEREFORE DESIGN IS OK.

APPENDIX 3-B

STORM WATER SYSTEM DESIGN CALCULATIONS

USE RATIONAL FORMULA TO CALCULATE SURFACE WATER RUNOFF.

$$Q = CiA$$

Q = RATE OF RUNOFF IN CFS
C = RUNOFF COEFFICIENT
i = AVERAGE RAINFALL INTENSITY, INCHES/HR
A = DRAINAGE AREA (ACRES) TRIBUTARY TO POINT UNDER DESIGN

ASSUMPTIONS:

- DRAINAGE STRUCTURES ARE SIZED FOR A 25 YEAR, 24 HOUR STORM AS REQUIRED BY THE NYSDEC

- HYDROLOGIC SOILS GROUP: D - CLAYEY SOIL WITH HIGH RUNOFF POTENTIAL, OPEN SPACE CONDITIONS FROM STORM DRAINAGE DESIGN MANUAL, ERIE & NIAGARA COUNTIES REGIONAL PLANNING BOARD, OCT 1, 1981 - EXHIBIT III-2 ATTACHED

BY TJR DATE 2/89 SHEET NO. 2 OF 8
CHKD. BY KRM DATE 2/89 JOB NO. 0605-12-1
SUBJECT APPENDIX 3-B

RUNOFF COEFFICIENT WAS DETERMINED BY ASSUMING:

- FROM DIRECT MEASUREMENTS OF USGS MAP OF GOWANDA, THE TOTAL DRAINAGE AREA INCLUDING OFF-SITE PROPERTY IS 2,000,000 FT^2
- FROM PLANIMETER MEASUREMENTS, LANDFILL AREA IS 1,162,000 FT^2 OR APPROXIMATELY 1/2 THE TOTAL DRAINAGE AREA
- OFF-SITE PROPERTY SLOPES > 6%

∴ FOR EACH ACRE MEASURED ON-SITE, ASSUME THAT AN EQUAL AREA OF OFF-SITE LAND DRAINS ONTO IT @ A >6% SLOPE

WEIGHTED COEFFICIENTS FOR SUB-AREAS WERE DETERMINED BY USING VALUES DEPENDENT ON THE SLOPE OF THE GROUND SURFACE. FOR AREAS HAVING VARIOUS SLOPES, AN INTERPOLATED VALUE WAS ASSIGNED BASED ON THE FOLLOWING SLOPED AREA RATIO:

$$C_{(\text{SUB-AREA})} = \Sigma \left(\begin{array}{c}\text{PERCENTAGE OF LAND}\\ \text{IN AREA OF CONCERN}\end{array}\right)\left(\begin{array}{c}\text{COEFFICIENT CORRESPONDING}\\ \text{TO SLOPE}\end{array}\right)$$

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BY TJR DATE 2/89 SHEET NO. 3 OF 8

CHKD. BY KRM DATE 2/89 JOB NO. 0605-12-1

SUBJECT APPENDIX 3-B

① CALCULATE PEAK Q @ POINT "C"

A) ON-SITE FLOW

AREA 1 SLOPES BETWEEN 2-6%

∴ C = 0.27 (EXHIBIT III-2)

RAINFALL INTENSITY = i = 0.161 in/hr (EXHIBIT III-6)

PEAK DISCHARGE = Q = CiA

= (0.27)(0.161) 2.03

= 0.09 CFS

B) OFF-SITE FLOW

OFF-SITE SLOPES > 6% ∴ C = 0.39 (EXHIBIT III-2)

RAINFALL INTENSITY = 0.161 in/hr

PEAK DISCHARGE = CiA

= (0.39)(0.161) 2.03

= 0.13 CFS

C) TOTAL FLOW @ POINT "C" = ON-SITE + OFF-SITE

= 0.09 + 0.13

= 0.22 CFS

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BY TJR DATE ...... SHEET NO. 4 OF 8

CHKD. BY KEM DATE 2/89 JOB NO. 0605-12-1

SUBJECT APPENDIX 3-B

② CALCULATE PEAK FLOW @ POINT "A"

A) <u>ON-SITE FLOW</u>

AREA	ACRES	RUNOFF COEFF (C)	PERCENTAGE OF TOTAL AREA WITH C
AREA 1 (2-6%)	6.53	0.27	$\frac{14.79}{1.0} = \frac{6.53}{x}$ x = 0.44
AREA 2 (2-6%)	7.82	0.27	$\frac{14.79}{1.0} = \frac{7.82}{x}$ x = 0.5
AREA 2 (> 6%)	0.44	0.39	$\frac{14.79}{1.0} = \frac{0.44}{x}$ x = 0.03
TOTAL	14.79		

$$C_{composite} = (0.44)(0.27) + (0.53)(0.27) + (0.03)(0.44)$$

$$= 0.12 + 0.14 + 0.01$$

$$= 0.27$$

RAINFALL INTENSITY = 0.161 in/hr (EXHIBIT III-6)

$$Q_{on\text{-}site} = CiA = (0.27)(0.161)(14.79)$$
$$= 0.64 \text{ CFS}$$

B) <u>OFF-SITE FLOW</u>

OFF-SITE SLOPES > 6% ∴ C = 0.39 (EXHIBIT III-

RAINFALL INTENSITY = i = 0.161 (EXHIBIT III-6)

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BY TJR DATE SHEET NO. 5 OF 8

CHKD. BY KPm DATE 2/89 JOB NO. 0605-12-1

SUBJECT APPENDIX 3-B

$Q_{OFF-SITE} = CiA = (0.39)(0.161)14.79$

$= 0.93$ CFS

c) TOTAL FLOW @ POINT "A" = ON-SITE + OFF-SITE

= 0.64 + 0.93

= 1.57 CFS

D) CULVERT SIZING

TO BE CONSERVATIVE, ASSUME ALL FLOW AT POINT "A" ENTERS PIPE IN NW CORNER OF AREA 2.

SLOPE OF PIPE AT POINT "A" = 1.1% = 0.011

ASSUME PIPE IS 80% FULL, THEN $\frac{Y}{d_o} = 0.8$

Y= depth of flow

d_o = diameter of pipe

ASSUME PIPE DIAMETER = 12" (d_o = 1')

MANNINGS ROUGHNESS COEFF = 0.011
(SEE ATTACHED CMP MANUAL)

$\frac{AR^{2/3}}{d_o^{8/3}} = 0.3$ (SEE FIGURE 6-1, CHOW, ATTACHED)

$AR^{.667} = 0.3\,(d_o)^{2.67}$

$= 0.3\,(1)^{2.67}$

$= 0.3$ CFS FOR CIRCULAR PIPE

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MALCOLM PIRNIE, INC.

BY TJR DATE ________ SHEET NO. 6 OF 8

CHKD. BY KRm DATE 2/89 JOB NO. 0605-12-1

SUBJECT APPENDIX 3-B

$$Q = \frac{1.49}{n}\left(AR^{2/3}\right)M^{1/2} = \frac{1.49}{0.011}\left(0.3\right)\left(0.011\right)^{.5}$$

$$= 135.5\,(0.3)(0.105)$$

$$= 4.3 \text{ CFS}$$

SINCE Q_{CULVERT} (4.3 CFS) > $Q_{\text{DESIGN FLOW}}$ (1.57 CFS), A 12 INCH DIAMETER PIPE IS SUFFICIENT. HOWEVER, USE AN 18" CMP TO BE CONSERVATIVE.

③ CALCULATE PEAK FLOW @ POINT "B"

A) ON-SITE FLOW

SLOPE	ACRES	RUNOFF COEFF (C)	PERCENTAGE OF TOTAL AREA WITH C	
2-6%	1.08	0.27	$\frac{3.56}{1.0} = \frac{1.08}{x}$	$x = 0.30$
> 6%	2.48	0.39	$\frac{3.56}{1.0} = \frac{2.48}{x}$	$x = 0.70$
TOTAL	3.56			

$$C_{\text{COMPOSITE}} = (0.30)(0.27) + (0.70)(0.39)$$

$$= 0.08 + 0.27$$

$$= 0.35$$

RAINFALL INTENSITY = i = 0.161 in/hr (EXHIBIT III-6)

$$Q = CiA = (0.35)(0.161)\,3.56$$

$$= 0.20 \text{ CFS}$$

MALCOLM PIRNIE

MALCOLM PIRNIE, INC.

BY TJR DATE 2/89 SHEET NO. 7 OF 8

CHKD. BY KPm DATE 2/89 JOB NO. 0605-12-1

SUBJECT APPENDIX 3-B

B) OFF-SITE FLOW

SLOPES $> 6\%$ ∴ USE $C = 0.39$ (EXHIBIT III-2)

INTENSITY $= i = 0.161$ in/hr (EXHIBIT III-6)

$$Q = CiA = (0.39)(0.161)\,3.56$$
$$= 0.22 \text{ CFS}$$

C) TOTAL FLOW @ POINT "B" = ON-SITE + OFF-SITE

$$= 0.20 + 0.22$$
$$= 0.42 \text{ CFS}$$

D) CULVERT SIZING

SLOPE OF PIPE AT POINT "B" $= 2\% = 0.02$

ASSUME PIPE IS 80% FULL, THEN $\frac{Y}{d_0} = 0.8$

ASSUME PIPE DIAMETER = 12" ($d_0 = 1'$)

MANNINGS ROUGHNESS COEFF = 0.011
(SEE ATTACHED CMP MANUAL)

$$\frac{AR^{2/3}}{d_0^{8/3}} = 0.3$$ (SEE FIGURE 6-1, CHOW, ATTACHED)

$$AR^{.667} = 0.3(d_0)^{2.67}$$
$$= 0.3(1)^{2.67}$$
$$= 0.3 \text{ CFS}$$

MALCOLM PIRNIE

MALCOLM PIRNIE, INC.

BY TJR DATE 2/89 SHEET NO. 8 OF 8

CHKD. BY KRM DATE 2/89 JOB NO. 0605-12-1

SUBJECT APPENDIX 3-B

$$Q = \frac{1.49}{n}\left(AR^{2/3}\right) m^{1/2} = \frac{1.49}{0.011}\left(0.3\right)\left(0.02^{.5}\right)$$

$$= 135.5\,(0.3)\,0.14$$

$$= 5.7 \text{ CFS}$$

SINCE $Q_{CULVERT}$ (5.7 CFS) > $Q_{DESIGN\ FLOW}$ (1.6 CF
A 12 INCH DIAMETER PIPE IS SUFFICIENT. HOWEVER, TO BE CONSERVATIVE, USE AN 18" CMP INSTEAD.

④ CALCULATE PEAK FLOW AT POINT "D"

SLOPE IS BETWEEN 2-6%, SURFACE IS ASPHALT. THEREFORE C = 0.85 (SEE TABLE III-1, ATTACHED)

RAINFALL INTENSITY = i = 0.161 IN/HR (EXHIBIT III-

$Q = CiA = (0.85)(0.161)(2.03)$
$= 0.28$ CFS

EXISTING 12 INCH PIPE IS ADEQUATE

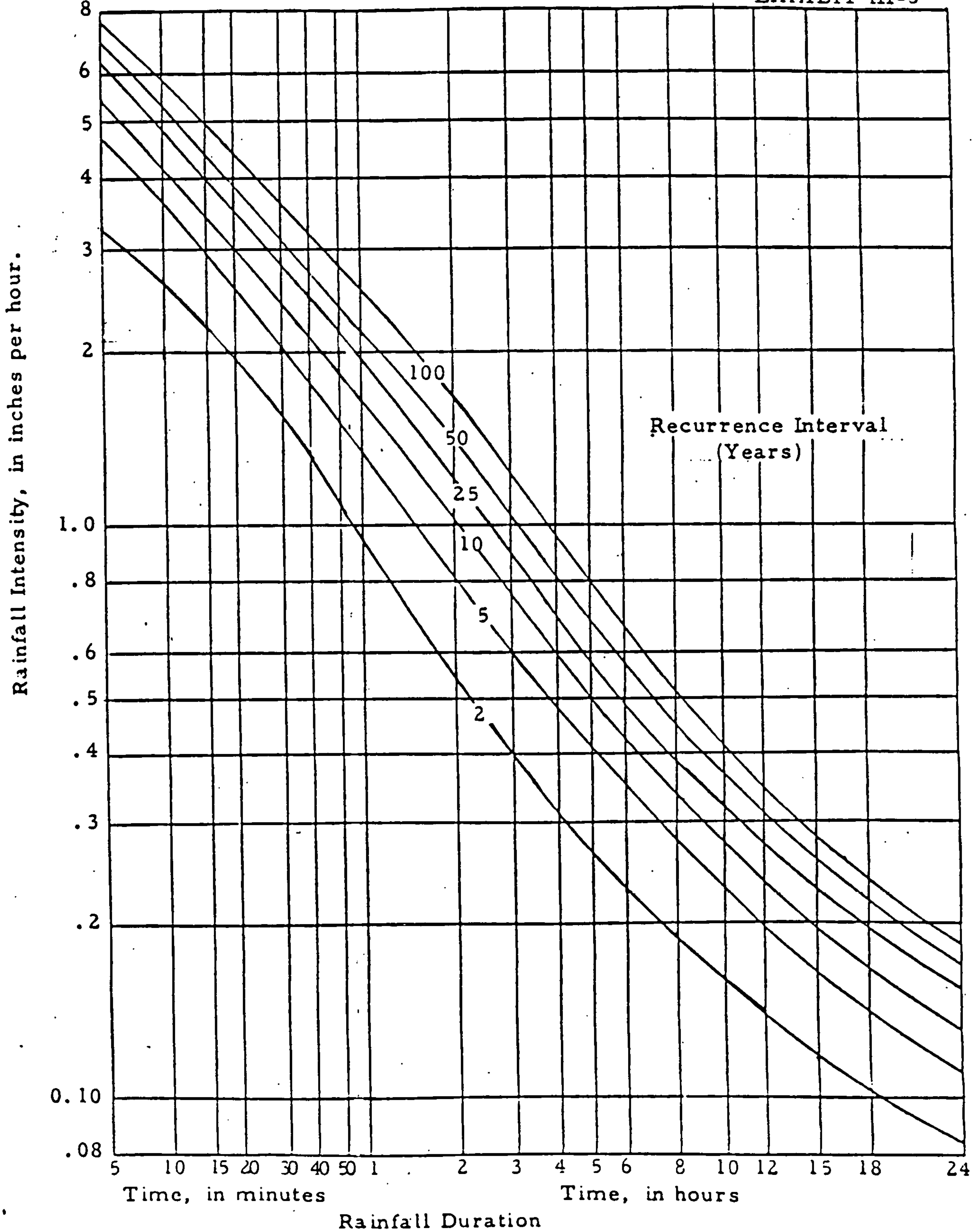
RUNOFF COEFFICIENTS *
FOR USE IN THE RATIONAL FORMULA

Hydrologic Soil Group	A			B			C			D		
Slope Range	0-2%	2-6%	6%+	0-2%	2-6%	6%+	0-2%	2-6%	6%+	0-2%	2-6%	6%+
LAND USE												
Industrial	0.67 1/	0.68	0.68	0.68	0.68	0.69	0.68	0.69	0.69	0.69	0.69	0.70
	0.85 2/	0.85	0.86	0.85	0.86	0.86	0.86	0.86	0.87	0.86	0.86	0.88
Commercial	0.71	0.71	0.72	0.71	0.72	0.72	0.72	0.72	0.72	0.72	0.72	0.72
	0.88	0.89	0.89	0.89	0.89	0.89	0.89	0.89	0.90	0.89	0.89	0.90
High Density 3/ Residential	0.47	0.49	0.50	0.48	0.50	0.52	0.49	0.51	0.54	0.51	0.53	0.56
	0.58	0.60	0.61	0.59	0.61	0.64	0.60	0.62	0.66	0.62	0.64	0.69
Medium Density 4/ Residential	0.25	0.28	0.31	0.27	0.30	0.35	0.30	0.33	0.38	0.33	0.36	0.42
	0.33	0.37	0.40	0.35	0.39	0.44	0.38	0.42	0.49	0.41	0.45	0.54
Low Density 5/ Residential	0.14	0.19	0.22	0.17	0.21	0.26	0.20	0.25	0.31	0.24	0.28	0.35
	0.22	0.26	0.29	0.24	0.28	0.34	0.28	0.32	0.40	0.31	0.35	0.46
Agricultural	0.08	0.13	0.16	0.11	0.15	0.21	0.14	0.19	0.26	0.18	0.23	0.31
	0.14	0.18	0.22	0.16	0.21	0.28	0.20	0.25	0.34	0.24	0.29	0.41
Open Space	0.05	0.10	0.14	0.08	0.13	0.19	0.12	0.17	0.24	0.16	0.21	0.28
	0.11	0.16	0.20	0.14	0.19	0.26	0.18	0.23	0.32	0.22	0.27	0.39
Freeways and Expressways	0.57	0.59	0.60	0.58	0.60	0.61	0.59	0.61	0.63	0.60	0.62	0.64
	0.70	0.71	0.72	0.71	0.72	0.74	0.72	0.73	0.76	0.73	0.75	0.78

1/ Lower runoff coefficients for use with storm recurrence intervals less than 25 years.
2/ Higher runoff coefficients for use with storm recurrence intervals of 25-years or more.
3/ High Density Residential - greater than 15 dwelling units per acre
4/ Medium Density Residential - 4 to 15 dwelling units per acre
5/ Low Density Residential - 1 to 4 dwelling units per acre

EXHIBIT III-2

EXHIBIT III-6



ERIE AND NIAGARA COUNTIES
REGIONAL PLANNING BOARD

REGIONAL STORM-SURFACE WATER
DRAINAGE MANAGEMENT STUDY

RAINFALL INTENSITY-DURATION-FREQUENCY, BUFFALO, NEW YORK

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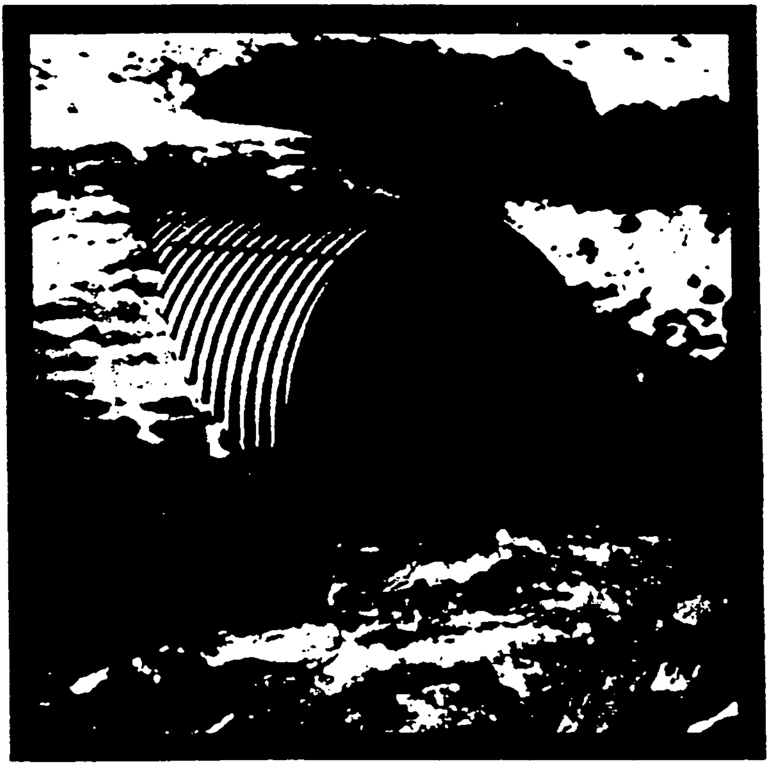
Source. U.S. Weather Bureau

NARZA ENGINEERING COMPANY . APRIL 1972

Corrugated steel pipe



culverts
sewers
construction products

CSP
CORRUGATED STEEL PIPE
STRENGTH–DURABILITY–ECONOMY

Technical Manual

Design of Sewers for Size

Storm sewers must be adequate to carry the runoff without flooding basements, streets, highways, parking lots and other areas. Runoff is computed by the Rational Method as on page 27.

Hydraulic fundamentals as they apply to sewer design can best be found in the many textbooks available on this subject.

The following quotation from the AISI "Handbook of Steel Drainage and Highway Construction Products," page 188, gives an interesting review of the various "energy losses" that are involved in a design of sewers:

Hydraulic Design of Sewers

The design of a sewer system is based on the total available energy and the losses of that energy that will occur from all causes in the total system. Conduit wall friction losses are usually a major source of energy loss, but the design of the pipe sizes cannot be properly based on this loss alone. The influence of other energy losses must be calculated and included in the overall design. In some systems such losses can be quite significant.

These "other" energy losses are commonly referred to as minor losses. Perhaps this terminology has caused them to be overlooked by designers on some occasions. These "minor" losses are caused by entrances, transitions, manholes and other junctions, elbows, bends, grade breaks, joints and misalignments. The energy lost is a function not only of geometry but water velocity. Thus, the velocity in the system will affect these energy losses.

A conduit with a higher "n" factor will have a higher energy loss in wall friction. However, this "rougher" conduit will also have a lower velocity of flow. The lower velocity will result in less energy loss from other sources. This should be taken into account in final sizing of the conduit rather than basing final pipe sizes only on wall friction charts.

Energy Losses

Energy losses result from two general causes—(1) changes in direction or magnitude of flow and (2) friction.

1. Change in Direction or Magnitude:

(a) **Entrance Losses** depend on the geometry of the inlet edge. See Table 30, page 29, for values of k_e for culverts. (values 0.2 to 0.9)

(b) Transitions in a manhole may vary from straight-through flow to change in direction or change in velocity of upstream and downstream conduits. k may vary from 0.5 for a sudden contraction to 0.1 for a well designed transition.

(c) Bends. A value of k_b of 0.4 is suggested for 90° circular bends where centerline radius exceeds pipe diameter.

(d) Junctions—where one or more branches enter a main sewer. Values of loss coefficients are not readily available.

2. Friction Loss:

The Manning Equation commonly used for sewer sizing is:

$$Q = \left(\frac{1.49}{n}\right) AR^{2/3} S^{1/2}$$

where Q = Discharge in cu ft per sec
A = Cross-sectional area of pipe, in sq ft
R = Hydraulic radius, in ft = area ÷ wetted perimeter
S = Slope of hydraulic grade line, in ft per ft
n = Coefficient of roughness of conduit interior (see Tables 31, 32 and 33)

Rearranged for energy loss in pipe friction, the equation is:

$$H_p\ (S) = \left(\frac{Q \times n}{1.49\ AR^{2/3}}\right)^2 \text{ in ft per ft of pipe}$$

The following charts in Figs. 19 through 22 can be used to find the friction energy loss for standard sizes of corrugated steel pipe for wall friction coefficients of .012 to .027.

Example

Given: Storm drain with three elbows and square-edge entrance box.
Length—750 feet Discharge 30 cfs
Maximum available head = 3.75 ft.
Loss coefficients k = 0.25 for elbow
k = 0.5 for entrance box

Required: Various alternate required sizes of smooth, annular and helical corrugated pipe.

Solution: 1. *Smooth Pipe:* reinforced concrete or fully lined corrugated steel pipe, n = 0.012

From Fig. 19, select tentative size of 30 in.

For 30-in., pipe friction energy loss = 750 x .0043 = 3.2 ft loss

$$V = \frac{Q}{A} = \frac{30}{4.9} = 6.1 \text{ fps}$$

Total of other losses:

$$H_L = \sum k\left(\frac{V^2}{2g}\right) = 3(0.25) + 0.5\left(\frac{6.1^2}{64.4}\right) = 0.72 \text{ ft loss}$$

Total loss = 3.2 + 0.7 = 3.9 ft

This exceeds the available head (3.75); try 36-in.

From Fig. 19, 36-in. pipe has loss = 750 x .0018 = 1.33 ft

Other losses will be less than for 30-in (0.72 ft)

Available head is 3.75 ft, so 36-in. pipe is obviously OK.

Result: *Use 36-in. smooth pipe.*

Solution: 2. *Annular Corrugated Pipe,* n = 0.024

From Fig. 21, select tentative size of 42-in.

For 42-in., pipe friction loss = 750 x 0.0032 = 2.4 ft loss

$$\text{For 42-in., } V = \frac{Q}{A} = \frac{30}{9.6} = 3.1 \text{ fps}$$

Total of other losses:

$$H_L = \sum k\left(\frac{V^2}{2g}\right) = 1.25 \times \left(\frac{3.1^2}{64.4}\right) = 0.19 \text{ ft loss}$$

Total loss = 2.4 + 0.19 = 2.6 ft

Result: Loss is less than available head. 42 in. is OK.

TABLE 33. COEFFICIENT OF ROUGHNESS — *n* FOR HELICALLY CORRUGATED PIPE

Corrugations	*1½" x ¼"*		*2⅔" x ½"*					*3" x 1"*					
Pipe Diameter	8"	10"	12"	18"	24"	36"	48"	36"	48"	54"	60"	66"	72"
Pipe Interior:													
Unpaved	.012	.014	.011	.014	.016	.019	.020	.021	.023	.023	.024	.025	.026
25% Paved					.015	.017	.020	.019	.020	.020	.021	.022	.022
Fully Paved					.012	.012	.012	.012	.012	.012	.012	.012	.012

SHEET 4 OF [illegible]

OPEN-CHANNEL HYDRAULICS

VEN TE CHOW, Ph.D.
Professor of Hydraulic Engineering
University of Illinois

McGRAW-HILL BOOK COMPANY
New York Toronto London
1959

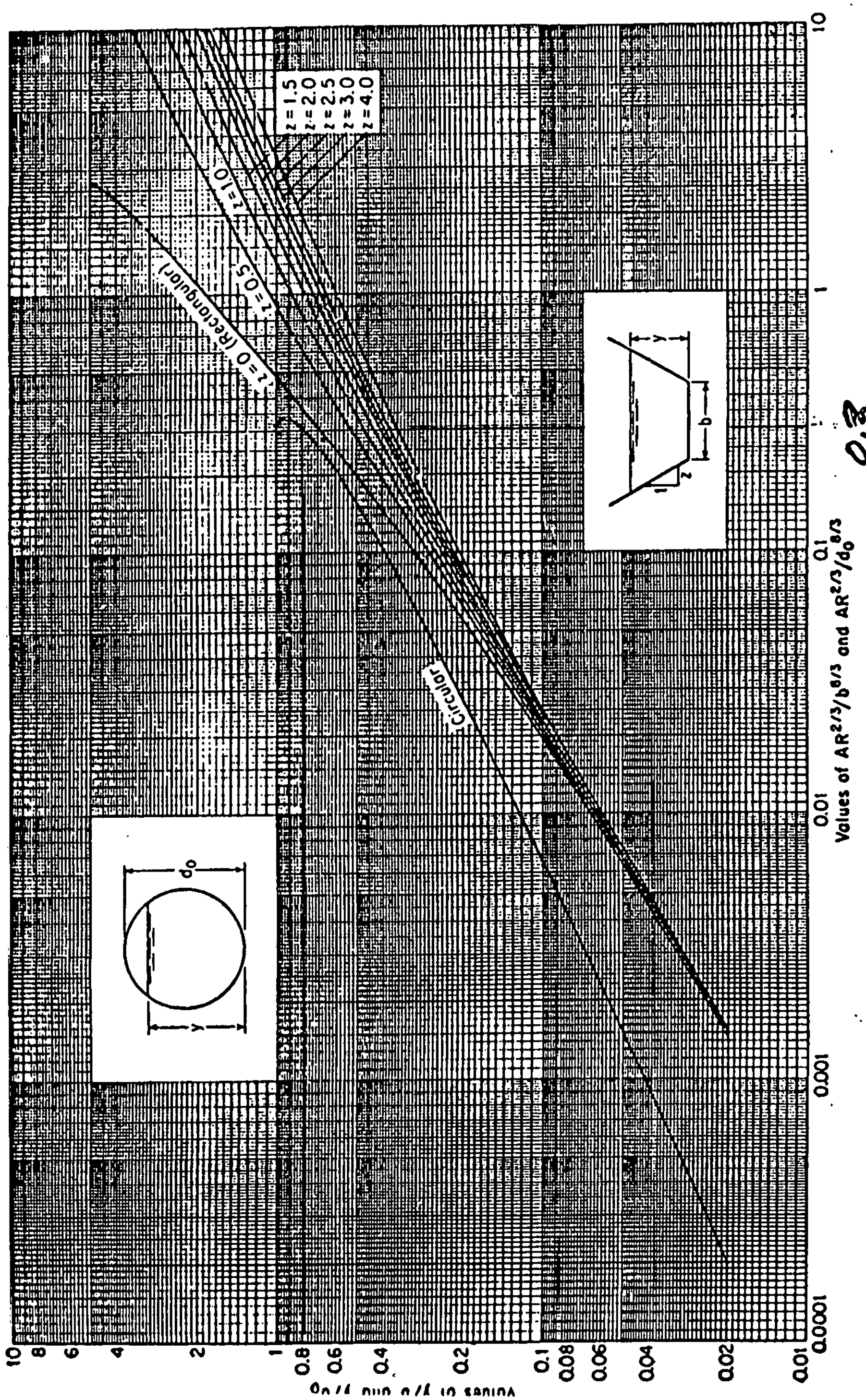


FIG. 6-1. Curves for determining the normal depth.

0.3

6-3. The Hydraulic Exponent for Uniform-flow Computation.

the conveyance K is a function of the depth of flow y, it may be ass that

$$K^2 = Cy^N$$

where C is a coefficient and N is a parameter called the *hydraulic exp for uniform-flow computation.*

From the logarithmic plotting of Eq. (6-10), it is evident tha hydraulic exponent N at depth y is

$$N = 2\frac{d(\ln K)}{d(\ln y)}$$

Now, taking logarithms on both sides of Eq. (6-6), $K = 1.49AR^{2/3}/n$ then differentiating this equation with respect to $\ln y$ under the ass tion that n is independent of y,

$$\frac{d(\ln K)}{d(\ln y)} = \frac{y}{A}\frac{dA}{dy} + \frac{2}{3}\frac{y}{R}\frac{dR}{dy}$$

Since $dA/dy = T$ and $R = A/P$, the above equation becomes

$$\frac{d(\ln K)}{d(\ln y)} = \frac{y}{3A}\left(5T - 2R\frac{dP}{dy}\right)$$

Equating the right sides of Eqs. (6-11) and (6-13) and solving fo

$$N = \frac{2y}{3A}\left(5T - 2R\frac{dP}{dy}\right)$$

This is the general equation for the hydraulic exponent N. trapezoidal channel section having a bottom width b and side slope z, the expressions for A, T, P, and R may be obtained from Tabl Substituting them in Eq. (6-14) and simplifying, the resulting equ is

$$N = \frac{10}{3}\frac{1 + 2z(y/b)}{1 + z(y/b)} - \frac{8}{3}\frac{\sqrt{1 + z^2}\,(y/b)}{1 + 2\sqrt{1 + z^2}\,(y/b)},$$

This equation indicates that the value of N for the trapezoidal sec a function of z and y/b. For values of z = 0, 0.5, 1.0, 1.5, 2.0, 2. and 4.0, a family of curves for N versus y/b can be const (Fig. 6-2).[2] These curves indicate that the value of N varies wi range of 2.0 to 5.3.

The curve for a circular section with N plotted against y/d_0, wl is the diameter, is also shown in Fig. 6-2. This curve shows th

---

[1] This equation [1] was also developed independently by Chugaev [2] thro use of the Chézy formula.

[2] Similar curves to those in Fig. 6-2 for trapezoidal channels were constru Kirpich [3] and also prepared independently by Pavlovskil [4] and Rakhmano

Group D - representing soils having a high runoff potential due to very slow infiltration rates. These soils consist primarily of clays with high swelling potential, soils with permanently high water tables, soils with a claypan or clay layer at or near the surface, and shallow soils over nearly impervious parent meterial.

A list of New York State soils and their hydrologic classification is presented in Exhibit III-1. Soils maps showing soil series names for specific ~~areas in the Region may be obtained from the SCS county offices.~~

(2) Land Use and Land Slope - Recommended C values for various types of impervious surfaces are given in Table III-1.

Table III-1

RECOMMENDED COEFFICIENT OF RUNOFF VALUES
FOR VARIOUS SELECTED IMPERVIOUS SURFACES

Surface	Runoff Coefficient
Streets	
Asphaltic	0.70 - 0.95 ←
Concrete	0.80 - 0.95
Drives & Walks	0.75 - 0.85
Roofs	0.75 - 0.95

Recommended C values for lawns and other unpaved and pervious areas are listed in Table III-2, and are specified by soil group and average land slope. The C values in Table III-2 are given as ranges because the rainfall-runoff relationship changes as the rainfall intensity changes. When designing for a high rainfall intensity with a return period of 25 years or more, the higher C values should be used; the lower C values should be used for a rainfall intensity having a return period less than 25 years. The soil group for a particular drainage area in Erie and Niagara Counties can be determined from detailed soil maps available from the Soil Conservation Service.

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APPENDIX 3-C

CONSTRUCTION QUALITY ASSURANCE (QA) PLAN FOR INSTALLATION OF THE FINAL COVER SYSTEM AT THE PALMER STREET LANDFILL

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CONSTRUCTION QUALITY ASSURANCE (QA) PLAN FOR INSTALLATION OF THE FINAL COVER SYSTEM AT THE PALMER STREET LANDFILL

MOENCH TANNING COMPANY
GOWANDA, NEW YORK

APRIL 1989

REVISED AUGUST 1989

MALCOLM PIRNIE, INC.

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0605-12-1

MALCOLM PIRNIE

CONSTRUCTION QUALITY (QA) PLAN
FOR INSTALLATION OF THE FINAL COVER SYSTEM
AT THE PALMER STREET SANITARY LANDFILL

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1.0 INTRODUCTION

This Quality Assurance (QA) Plan describes quality assurance procedures for the installation of the final cover system (viz. a twenty-four (24) inch barrier layer with twelve (12) inches of topsoil) on the Palmer Street Landfill (see Figure 1 for location). This QA Plan stresses careful inspection and documentation during the entire construction phase of the project, from the selection of materials through the installation of final cover.

All parties involved in this final cover system construction project have had input into and will receive a copy of this QA Plan including the Owner, Project Officer, Project Manager, Quality Assurance Engineer and the NYSDEC. They will also be given any other quality assurance documents specially prepared for the project, if any.

The overall goals of this QA program are to ensure that proper construction techniques and procedures are used, and to verify that the materials used meet the specifications. This QA Plan is designed as a supplement to the contract documents and is intended for use by the QA personnel only. Any conflicts between the contract documents and the QA Plan shall be brought to the immediate attention of the Owner and the QA Engineer. The contract documents shall govern unless otherwise directed by the QA Engineer. Additionally, the program will attempt to identify and define problems that may occur during construction and address corrective measures. After completion of the work, a construction monitoring report will be prepared which documents that the facility was constructed in general conformance with the design standards and specifications and identifies where and why the record drawings and constructed facilities were observed to deviate from the contract documents.

This QA Plan was prepared in accordance with the following:

- "Palmer Street Landfill Closure/Post-Closure Plan" prepared by Malcolm Pirnie, Inc. and approved by the New York State Department of Environmental Conservation (NYSDEC).

- "Construction Quality Assurance for Hazardous Waste Land Disposal Facilities", EPA/530-SW-86-031 United States Environmental Protection Agency.

2.0 SCOPE

The work addressed under this QA Plan will facilitate proper construction of the final cover system for the Palmer Street Landfill. All work will be constructed to the lines, grades, and dimensions indicated on the plans and details, and in accordance with the project specifications and/or closure plan or as may otherwise be required by the Owner or Malcolm Pirnie, Inc. (Engineer).

Inspectors will issue a daily report of activities at the site. These reports will include, at a minimum, observations and test results, as well as problems encountered and solutions achieved.

3.0 RESPONSIBILITY AND AUTHORITY

3.1 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) MANAGEMENT ORGANIZATION

The principal organizations involved in permitting, designing and constructing the final cover system for the Palmer Street Landfill facility include the New York State Department of Environmental Conservation (NYSDEC), Moench Tanning Co. (the facility owner/operator), the construction contractor, and Malcolm Pirnie, Inc. (the design engineer and QA personnel).

3.1.1 New York State Department of Environment Conservation (NYSDEC)

It is the responsibility of the NYSDEC to review the facility owner's Closure/Post-Closure Plan and final cover system design (including the construction QA Plan) for compliance with the agency's regulations and to make a decision to accept or reject the final cover system construction based on this review. The NYSDEC will have the responsibility and authority to review, and accept or reject any design revisions or requests for a variance that are submitted by Moench Tanning Co. and/or the Design Engineer. The agency also has the responsibility and authority to review and approve the Construction Monitoring Report and all QA documentation collected during the final cover system construction to confirm that the approved QA Plan was followed and that the final cover system was constructed as specified in the contract documents.

3.1.2 Moench Tanning Company

Moench Tanning Company is responsible for the design and construction of the final cover system for the Palmer Street Landfill facility. This responsibility includes complying with landfill construction Quality Control (QC) requirements of the NYSDEC. Moench Tanning Company has the authority to monitor and control the quality of construction and related activities in full conformance with the design plans and specifications and the approved Closure/Post-Closure Plan. Moench Tanning also has the authority to select professional organizations to assist them in fulfilling these responsibilities.

3.1.3 Malcolm Pirnie, Inc.

Malcolm Pirnie, Inc. will be responsible for engineering design changes, material inspection, construction inspection and quality assurance in accordance with this QA Plan. Malcolm Pirnie, Inc. will inform all parties involved with construction of their responsibilities, lines of communication, lines of authority, and quality assurance/quality control procedures. Malcolm Pirnie, Inc. QA personnel will monitor closure construction activities. QA personnel will be assigned specific responsibilities and tasks. All field and laboratory testing and monitoring will be performed by Malcolm Pirnie, Inc., at a frequency and manner specified in this QA Plan. In the event that scheduling problems necessitate use of a soils testing subcontractor, the NYSDEC will be notified. QA personnel will include a Project Officer, Project Manager, QA Engineer, Soils Lab Director and the necessary supporting engineering and inspection personnel. Specific QA responsibilities of the Project Officer will include:

- Overall technical quality assurance;
- Certifications, on behalf of Malcolm Pirnie, Inc., that the construction was completed in general conformance with the approved Closure Plan, design plans and specifications; and
- Supporting the QA Engineer in meetings with the NYSDEC, as necessary.

Specific responsibilities of the Project Manager will include:

- Reviewing design criteria, plans, and specifications for clarity and completeness so that the QA Plan can be implemented;
- Supporting the QA Engineer in meetings with the NYSDEC, as necessary;
- Consulting with the QA Engineer on field problems and corrective measures;
- Scheduling and coordinating QA inspection activities; and
- Witness critical aspects of construction work, as necessary.

Specific responsibilities of the QA Engineer will include:

- Serving as the primary interface with NYSDEC personnel;
- Directing and supporting the QA inspection personnel in performing observations and tests by:
    - o confirming that regular calibration of testing equipment is properly conducted and recorded,
    - o confirming that the testing equipment, personnel, and procedures do not change over time or making sure that any changes do not adversely impact the inspection process,
    - o confirming that the test data are accurately recorded and maintained, and
    - o verifying that the raw data are properly recorded, validated, reduced, summarized, and interpreted;
- Informing Project Manager of problems or deficiencies, if any;
- Weekly site visits to review the adequacy of completed work;

- Witnessing all critical aspects of construction work:
  - o The QA Engineer and/or a licensed Professional Engineer will, at a minimum, observe the following, prior to burial:
    - subgrade preparations,
    - barrier layer test patch construction,
    - ditch (between Areas 1 and 2) construction,
    - barrier layer completion prior to topsoil placement, and
    - infiltrometer installations;
- Prompt inspection of suspected non-standard work when notified by QA inspection personnel; and
- Providing reports to Moench Tanning Co. on the inspection results including:
  - o review and interpretation of all data sheets and reports,
  - o identification of work that he/she believes should be accepted, rejected, or uncovered for observation, or that may require special testing, inspection, or approval, and
  - o rejection of defective work and verification that corrective measures are implemented.

Specific responsibilities of the Soils Laboratory Director include:

- Coordinating activities with the QA Engineer and supporting QA inspection personnel regarding the collection and analysis of soil samples;
- Scheduling and quality assurance of all soil analyses; and
- Informing the QA Engineer of materials that are not of acceptable quality or that fail to meet specifications.

For the supporting QA inspection personnel, specific responsibilities will include:

- Performing independent, continuous, on-site inspection of the work in progress to assess compliance with the facility design criteria, plans, and specifications;

- Verifying that the equipment used in testing meets the test requirements and that the tests are conducted according to this QA Plan; and
- Reporting to the QA Engineer results of all inspections including work that is not of acceptable quality or that fail to meet the specified design.
- Inspect and verify that labels, tags, manifests, or other identifying documents of all construction materials conform to material specifications.

3.2 PROJECT MEETINGS

Conducting periodic project meetings is the responsibility of Malcolm Pirnie, Inc. and Moench Tanning Company.

3.2.1 Preconstruction Meeting

A preconstruction meeting will be held prior to construction of the facility's final cover system. Representatives of Moench Tanning, Malcolm Pirnie, Inc., the NYSDEC and the construction contractor will be present. The agenda for this meeting will include but not be limited to the following:

- Provide each organization with all relevant QA documents and supporting information;
- Familiarize each organization with the QA Plan and its role relative to the design criteria, closure plans, specifications and construction documentation;
- Determine if any changes to the QA Plan are needed to ensure that the final cover system will be constructed to meet or exceed the specified design;
- Review the responsibilities of each organization;
- Review lines of authority and communication for each organization;
- Discuss the established procedures or protocol for observations and tests including sampling strategies;
- Discuss the established procedures or protocol for handling construction deficiencies, repairs, and retesting;

- Review methods for documenting and reporting inspection data;
- Review methods for distributing and storing documents and reports;
- Review work area security and health and safety protocol;
- Discuss procedures for the location and protection of construction materials and for the prevention of damage of the materials from inclement weather or other adverse events; and
- Conduct a site walk-around to review construction material and inspection equipment storage locations.

3.2.2 Monthly Progress Meetings

Monthly progress meetings will be held during the course of the work to:

- Discuss the project schedule and work performed to date;
- Address and resolve (viz. establish corrective actions for) any existing or anticipated construction problems; and
- Discuss and resolve (viz. establish corrective actions for) any coordination or QA problems encountered to date.

The meetings will be attended by Moench Tanning Co. personnel, Malcolm Pirnie, Inc. QA personnel and the construction contractor. The NYSDEC will also be advised of the meeting time and place. The meetings will be scheduled one month in advance. The meeting minutes will be documented by a member of Malcolm Pirnie, Inc. QA personnel.

3.2.3 Problem or Work Deficiency Meetings

A special meeting will be held when and if a major QA problem or deficiency is present or likely to occur. At a minimum, the meeting shall be attended by the construction contractor, QA inspection personnel, and the QA Engineer. NYSDEC personnel will also be informed of the meeting time and place. The purpose of these meetings will be to define and resolve the QA problem(s) encountered or recurring QA deficiencies in the following manner:

- Define and discuss the problem or deficiency;

- Define and discuss the problem or deficiency;

- Review alternative solutions; and
- Implement a plan to resolve the problem or deficiency.

The meeting minutes will be documented by a member of Malcolm Pirnie, Inc. QA personnel.

3.3 PROJECT SCHEDULE

A general construction schedule for closure activities is provided in Appendix A. A schedule that indicates the construction activities time frame, task phases, critical construction items, progress meetings, and progress reports will be prepared by the Contractor and submitted to the NYSDEC prior to initiation of any work. In the event construction activities are delayed due to unforseen circumstances such as problem situations, inclement weather, mechanical equipment breakdown, etc., the schedule shall be revised accordingly and will accompany the weekly reports submitted to the NYSDEC.

In conjunction with the construction schedule, the NYSDEC will be notified (by telephone) approximately 24 hours prior to the anticipated completion of the following construction activities:

- subgrade preparations;
- barrier layer test patch construction;
- ditch (between Areas 1 and 2) construction;
- barrier layer completion prior to topsoil placement; and
- infiltrometer installations.

These critical construction items will not be buried or obscured from NYSDEC supplemental inspection for 48 hours after completion.

Placement and compaction of earthen materials shall not be performed after November 30 and before April 1, or during any other times when adverse weather conditions exist without express written approval from the

NYSDEC. Adverse weather conditions typically include extended moderate to heavy rainfall, moderate to heavy snowfall, and extended freezing periods. If it is deemed necessary to continue earthwork construction during the above periods, a request to perform adverse weather construction permit shall be submitted. This request shall include, at a minimum, the following:

- a revised construction schedule;
- a statement of expected prevailing weather conditions;
- a description of any special construction procedures and/or materials that may be utilized; and
- a description of any recommended special quality assurance/quality control procedures.

4.0 MALCOLM PIRNIE, INC. QUALIFICATIONS

4.1 GENERAL

Malcolm Pirnie, Inc. is one of the nation's leading consulting firms in the fields of environmental engineering, science and planning. Established in the early 1900s, the firm has grown steadily over the years and has achieved wide recognition for the consistent quality and innovation exhibited by our ideas, plans, designs, and the performance of our completed projects.

Malcolm Pirnie, Inc. has headquarters in White Plains, New York and offices in Albany, Syracuse and Buffalo, New York in addition to many other locations throughout the United States. Malcolm Pirnie, Inc. provides complete environmental consulting services - from permitting and investigations through design, construction administration, and operations assistance - for the management of solid and hazardous wastes and other environmental fields.

Malcolm Pirnie, Inc. has been involved in many significant land disposal projects for municipal and industrial clients as well as government agencies. Malcolm Pirnie, Inc. has extensive experience in the siting, permitting, design, and construction administration of landfills, leachate collection and treatment systems, and the expansion and closure of landfills.

A table of Malcolm Pirnie's representative landfill experience in New York State is presented as Table 1.

4.2 DESIGNATED QA PERSONNEL

Implementation of the QA plan including certification that construction activities were completed in general conformance with the design criteria, plans and specifications are the responsibility of Malcolm Pirnie, Inc. The Malcolm Pirnie, Inc. personnel designated for involvement in this project (see Figure 2 for Organizational Chart) are as follows:

Project Officer	-	Paul H. Werthman, P.E.
Project Manager	-	Wesley C. Dust, P.E.
QA Engineer:		
Primary	-	Terry Ried
Backups	-	Wesley C. Dust, P.E.
	-	Kent R. McManus, P.E.
Soils Laboratory Director	-	Anne Marie C. McManus, P.E.

Resumes of these personnel are provided in Appendix E. All designated personnel are subject to change as required to facilitate completion of the construction activities. The NYSDEC will be notified when any of the above-designated personnel are changed.

4.3 QA INSPECTION PERSONNEL

The person(s) filling this position will be trained and certified to operate a nuclear densitometer. He/they will also be Health and Safety trained. They will have a working knowledge of documents pertaining to construction of the final cover system for the Palmer Street Landfill, including the Closure/Post-Closure Plan, the Contract Documents, and this

TABLE I

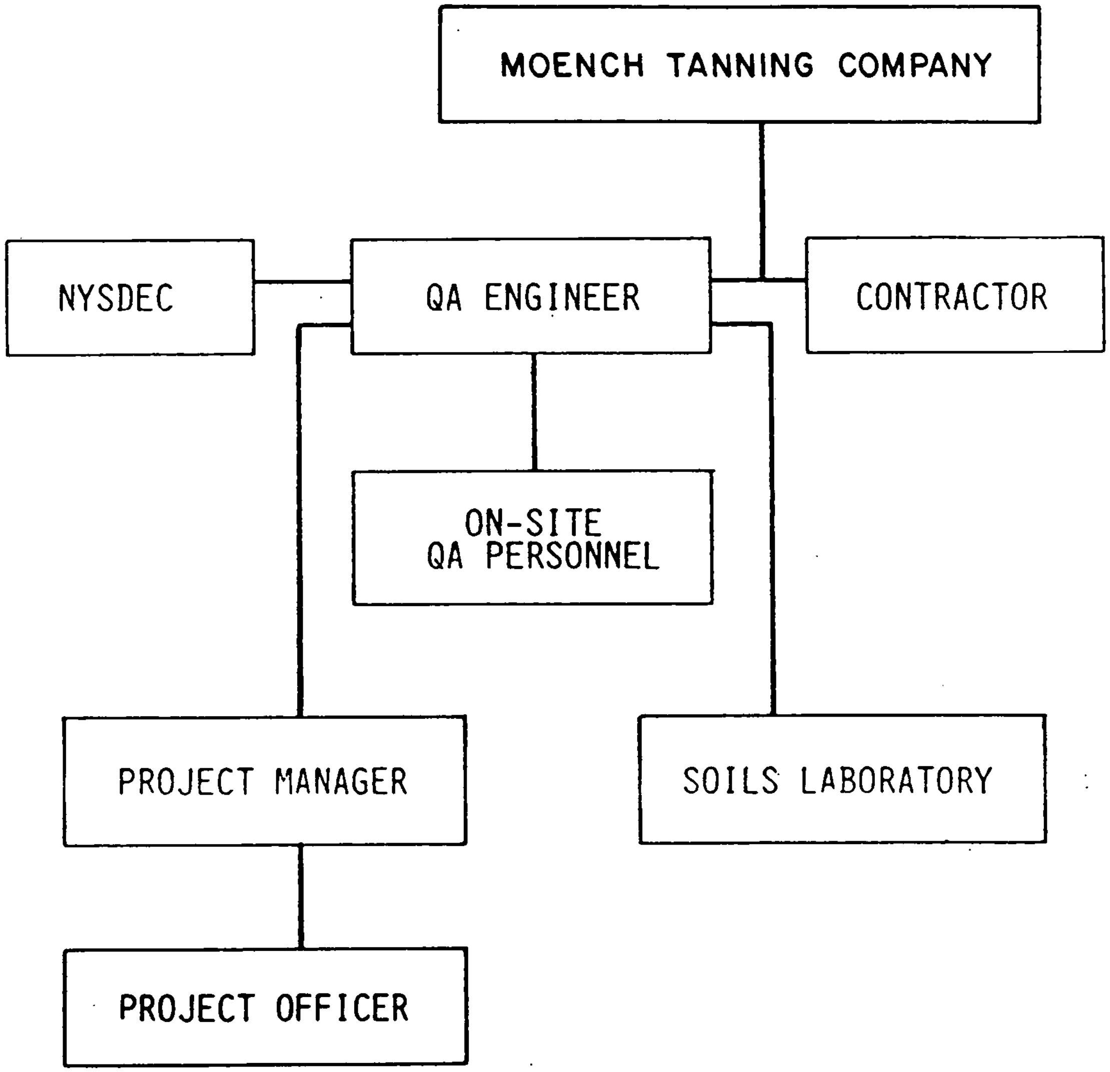
CLIENT	TYPE OF LANDFILL				INVESTIGATION					ENVIRONMENTAL ASSESSMENT/ PERMITTING							DESIGN/CLOSURE										CONSTRUCTION		
	CONS. & DEM. DEBRIS	SANITARY	SPECIAL PURPOSE	HAZARDOUS WASTE	GEOPHYSICAL	SUBSURFACE SOILS	MONITORING WELLS	SITE ASSESSMENT	GROUND WATER SAMPLING	EAF/EIS	PUBLIC PARTICIPATION	ORDER ON CONSENT	SPDES PERMIT	PART 360 PERMIT	MINING PERMIT	VARIANCES	SOIL LINER	SYNTHETIC LINER	LEACHATE COLLECTION/ LEAK DETECTION	LEACHATE STORAGE/ TREATMENT	GAS MIGRATION MANAGEMENT	SOIL CAPPING	SYNTHETIC CAPPING	OPERATION PLAN	CLOSURE/POST-CLOSURE PLAN	CAPPING AND LINER QA/QC	SOILS TESTING	INSPECTION/ CERTIFICATION	
CATTARAUGUS COUNTY																													
• FIVE POINTS LANDFILL CLOSURE	⊗					⊗	⊗		⊗	⊗		⊗			⊗				⊗	⊗	⊗	⊗		⊗	⊗	⊗	⊗	⊗	
• FARWELL LANDFILL CLOSURE		⊗				⊗	⊗	⊗	⊗		⊗	⊗							⊗	⊗	⊗	⊗			⊗	⊗	⊗	⊗	
V-COWANDA LANDFILL CLOSURE	⊗					⊗	⊗		⊗												⊗	⊗			⊗	⊗	⊗	⊗	
T-BATAVIA LANDFILL CLOSURE		⊗				⊗	⊗		⊗			⊗							⊗	⊗	⊗	⊗			⊗	⊗	⊗	⊗	
C-NIAGARA FALLS WW SLUDGE SITE			⊗			⊗	⊗	⊗	⊗	⊗	⊗			⊗		⊗			⊗	⊗	⊗	⊗			⊗				
T-AMHERST WW SLUDGE SITE			⊗			⊗	⊗	⊗	⊗	⊗									⊗	⊗	⊗	⊗			⊗				
CONF. CLIENT NO. 0848 SLAG SITE	⊗		⊗			⊗	⊗		⊗												⊗	⊗			⊗				
CONF. CLIENT NO. 0848 BOF DUST SITE				⊗		⊗	⊗		⊗												⊗		⊗		⊗				
FORMSO LANDFILL CLOSURE		⊗				⊗	⊗		⊗	⊗		⊗		⊗	⊗				⊗	⊗	⊗	⊗		⊗	⊗	⊗	⊗	⊗	
CONF. CLIENT NO. 0605 SLUDGE LANDFILL			⊗		⊗	⊗	⊗		⊗	⊗				⊗	⊗	⊗	⊗	⊗	⊗	⊗	⊗	⊗		⊗	⊗	⊗	⊗	⊗	
CONF. CLIENT NO. 0605 LANDFILL CLOSURE				⊗	⊗	⊗	⊗	⊗	⊗	⊗	⊗										⊗	⊗			⊗	⊗			
NM. MOHAWK-DUNKIRK LANDFILL DESIGN			⊗			⊗	⊗	⊗		⊗	⊗		⊗	⊗		⊗	⊗	⊗	⊗			⊗		⊗	⊗	⊗			
NM. MOHAWK HUNTLEY LANDFILL DESIGN			⊗			⊗	⊗		⊗					⊗		⊗	⊗		⊗			⊗			⊗				
CONF. CLIENT NO. 740 LANDFILL CLOSURE	⊗			⊗		⊗													⊗			⊗			⊗				
T-NORTH HEMPSTEAD PORT WASHINGTON LANDFILL DESIGN		⊗				⊗	⊗				⊗	⊗	⊗	⊗				⊗	⊗	⊗	⊗		⊗	⊗	⊗	⊗	⊗	⊗	
T-ISLIP LANDFILL EXPANSION		⊗					⊗	⊗				⊗		⊗				⊗	⊗	⊗	⊗		⊗	⊗	⊗	⊗	⊗	⊗	
T-ISLIP LANDFILL DESIGN			⊗				⊗	⊗				⊗		⊗				⊗	⊗	⊗	⊗		⊗	⊗	⊗	⊗	⊗	⊗	
T-WORCESTER LANDFILL CLOSURE		⊗										⊗					⊗				⊗	⊗		⊗	⊗	⊗			
C-ALBANY LANDFILL DESIGN		⊗	⊗		⊗	⊗	⊗	⊗	⊗	⊗	⊗	⊗		⊗				⊗	⊗	⊗	⊗		⊗	⊗	⊗				
WESTCHESTER COUNTY SPROUT BROOK LANDFILL DESIGN			⊗		⊗	⊗	⊗	⊗	⊗	⊗	⊗		⊗	⊗	⊗			⊗	⊗			⊗		⊗	⊗				
NEWTON FALLS PAPER MILL, INC. LANDFILL CLOSURE & PERMITTING			⊗		⊗	⊗	⊗	⊗	⊗	⊗	⊗	⊗	⊗	⊗			⊗	⊗	⊗	⊗		⊗		⊗	⊗				
STEUBEN COUNTY																													
• T-BATH NEW LANDFILL CONSTRUCTION		⊗																								⊗	⊗	⊗	
T-NISKAYUNA LANDFILL CLOSURE	⊗	⊗					⊗	⊗				⊗							⊗	⊗	⊗	⊗	⊗	⊗	⊗	⊗	⊗	⊗	

MALCOLM PIRNIE

REPRESENTATIVE EXPERIENCE SUMMARY
LANDFILL DESIGN AND CLOSURE
IN NEW YORK STATE

MOENCH TANNING COMPANY
PALMER STREET LANDFILL
QA

FIGURE 2



MOENCH TANNING COMPANY
PALMER STREET LANDFILL

QA ORGANIZATIONAL CHART

MALCOLM PIRNIE

QA Plan. In addition, field personnel will be instructed to contact QA Engineer in the event closure requirements are not being met, QA procedures are not being implemented, or construction problems have been encountered.

5.0 INSPECTION ACTIVITIES

5.1 EARTH MATERIALS QUALITY ASSURANCE

5.1.1 General

The final cover system (which will consist of a 24-inch barrier layer of recompacted soil and 12-inches of topsoil) for the Palmer Street Landfill is designed to provide long-term minimization of liquid migration and leachate formation in the closed landfill by limiting the infiltration of surface water into the facility for the post-closure period. The final cover system will be constructed so that it functions with minimum maintenance, promotes drainage and minimizes erosion of the cover. It will also accommodate settlement and subsidence so that the cover's integrity is maintained.

Criteria used for placing barrier layer soil material during cover system construction are defined in the project specifications. The following construction guidelines shall be followed:

- The subgrade will be uniformly graded to lines and grades depicted on construction grading plans and will be free of soft or wet areas;

- Final subgrade preparation will require approval by the QA Engineer prior to placing barrier layer soil;

- Barrier layer soil will be placed in loose lifts between a minimum thickness of six (6) inches and a maximum of nine (9) inches;

- Barrier soil will be compacted with tamping foot or sheepsfoot rollers. Minimum length for sheepsfoot compacting feet will be maintained at six (6) inches and in no case will be less than the loose lift thickness in order to promote effective compaction;

- Compacted barrier layer soil zones will be not less than ten (10) feet in width or greater than 500 feet in length and will be compacted across the entire width;

- Intermediate lifts will be seal rolled when subsequent lifts will not be placed within 48 hours of completion;

- Sealed intermediate lifts will be scarified and if necessary, moistened prior to placement of subsequent barrier layer soil lifts;

- Damage to compacted lifts (viz. rutting by equipment) will be repaired prior to placing any overlying materials;

- If necessary, irregular surfaces and contours will be cut back ✓ ~~or modified to design grades and lines;~~ TO ACHIEVE UNIFORM GRADES AND LINES

- The barrier layer soil moisture content will be maintained greater than optimum during placement and compaction, and when necessary, the moisture content will be adjusted accordingly using practical field equipment and methods;

- Compaction of barrier layer soil containing excessive moisture will not be attempted until the soil moisture content is dried to an acceptable moisture content;

- Deposited barrier soil piles for placement will not exceed one (1) rank beyond the spreading face; and

- No area shall receive less than or more than twice the predicted (based on the test patch) number of passes to reach the required density. In no case shall an over-compacted crust be formed on the top of the lift. The predicted number of passes may be altered based on adjusted field or soil conditions. The NYSDEC will receive notification and appropriate justification prior to adjusting the predicted number of passes.

Assurance that construction of the final cover system for the Palmer Street Landfill is in accordance with the project closure plans, specifications and/or NYSDEC requirements shall be accomplished by the judicious use of quality assurance testing.

5.1.2 Barrier Layer

Specific quality control testing for the recompacted soil barrier layer shall consist of material evaluations and construction quality evaluations. Barrier layer soil evaluation data will be submitted to the

NYSDEC and will be included in the weekly reports. Each is discussed in more detail below.

5.1.2.1 Material Evaluations

Material evaluations shall be performed on mined and stockpiled soil proposed for use to ascertain its acceptability as construction material and compliance with the closure plans and specifications. Approximately 108,000 cubic yards of material will be mined for use in constructing the barrier layer. This QA plan assumes that all barrier layer soil will be obtained from one source (i.e. Moench Tanning's Point Peter Road Site). If an alternative borrow source is identified, the NYSDEC will be notified and the QA procedures will be modified (subject to approval by NYSDEC) prior to its use.

Barrier layer soil material is a relatively low permeability soil free from roots, organic matter, trash, debris, and other deleterious materials. Barrier layer soil will be screened to remove 3 inch or larger rock, stone and debris; and then stockpiled for QA laboratory testing. In addition, visible accumulations of undesirable material i.e. stone or rock greater than one (1) inch in size during soil placement shall be removed and replaced prior to compaction.

Criteria to be used for determining the acceptability of materials for use during construction are defined in the project specifications approved by the NYSDEC. All evaluation tests will be performed in Malcolm Pirnie's soils testing laboratory. The testing frequency and sampling protocols are discussed as sections 5.1.4 and 6.0, respectively.

The following tests will be performed to facilitate material evaluations:

Test	ASTM Standard No.
- Water (Moisture) Content of Soil and Soil Aggregate	D2216-80
- Gradation Analysis of Soils (Sieve and Hydrometer)	D422-63
- Atterberg Limits	D4318-83

- Moisture Density Relations of Soil and Soil Aggregate Mixtures Using 10-lb. Rammer and 18-in. Drop (Modified Proctor)	D1557-78
- Moisture-Density Relations of Soils and Soil-Aggregate Mixtures using 5.5 lb Rammer and 12-inch Drop (Standard Proctor)	D698-78
- Recompacted Laboratory Hydraulic Conductivity Testing at 90 Percent of the Modified Proctor Density on the Wet Side of Optimum Moisture Density Relations of Soil and Soil Aggregate Mixtures Using 10-lb. Rammer and 18-inch Drop (Modified Proctor)	(Current Literature-Appendix C-1)
- Moisture, Ash and Organic Matter of Peat and Other Organic Soils	D2974-87

a. Water Content

This test will be used to determine whether the soil proposed for use is wet or dry of the optimum water content (see Form A, Appendix B).

b. Gradation

The final cover material shall conform to the following gradation requirements:

Sieve Size Designation	Percent Minimum Passing by Weight
3 inches	100
No. 4	85
No. 200	50
0.002 mm	25

Soil material which does not meet this gradation may be rejected as final cover construction material depending on permeability testing results (see Forms A and B, Appendix B).

c. Atterberg Limits

Although Atterberg Limits will be monitored, they will not be used as criteria for rejection or acceptance of the soil material. Atterberg limits will help to classify the various soils encountered and, in correlation with other soil properties, will help to define the soil's behavior (such as permeability and compactability) (see Form A, Appendix B).

d. Moisture-Density Relationships

The moisture density relationships determined during the materials evaluation testing will be used as a basis for determining whether optimal moisture content and compaction is achieved during the construction quality evaluation. The QA inspector will program the nuclear densitometer with the Modified Proctor optimum moisture content and maximum dry density representative for the soil being placed (see Form C, Appendix B).

e. Recompacted Hydraulic Conductivity (Permeability)

Recompacted permeability of the soil being tested shall have a maximum value of 1.0×10^{-7} cm/sec. Soils which do not meet this requirement will be rejected (see Form D, Appendix B).

5.1.2.2 Construction Quality Evaluation

Construction quality evaluations will be performed on all components of the barrier layer construction as part of the certification program. Criteria to be used for determination of acceptability of the construction work will be as identified in the project closure plans and specifications.

Construction evaluation testing will consist of visual observations of the work, in-place soil density/moisture content checks, undisturbed hydraulic conductivity (permeability) testing, a survey of as-built conditions and a visual assessment of the adequacy of layer bonding.

a. Moisture Control

The QA inspector will check the moisture content of the final cover material using the nuclear densitometer programmed for the soil being placed. The final cover material moisture content shall be greater than optimum prior to compaction. Final cover material shall not be placed unless the moisture content of the previous lift or subgrade is between optimum and four percent (4%) greater than optimum. The current loose lift shall not be compacted unless the moisture content is greater than optimum. When necessary, moisture will be added using approved sprinkling equipment. Construction personnel shall add sufficient water during rolling and tamping to assure complete compaction of material. If the material is too wet for satisfactory compaction, construction personnel shall temporarily stop work and the material will be allowed to dry. The placement or compaction of material will not be permitted during or immediately following rainfall. Construction of the final cover system shall be conducted in such manner that a minimum of rain water will be retained thereon. Compacted material that is damaged by washout shall be replaced by construction personnel in an acceptable manner. The construction personnel will not be permitted to proceed with in-place soil compaction until the moisture content of the soil is approved by the QA personnel (see Form E, Appendix B).

b. <u>In-Place Soil Density Control</u>

Each layer of the final cover system will be compacted to a minimum of 90 percent of the modified proctor maximum density, in pounds per cubic foot, as determined by the Modified Proctor Compaction Test, ASTM D-1557-78; and in accordance with the procedures for determining the acceptable level of compaction as described in Appendix D. Construction personnel shall select equipment which is capable of providing the minimum densities required by the specifications and shall submit a description of the type of equipment proposed for use to the QA personnel for approval. Lift thicknesses, water content (of the material), compactor weight and the number of passes of the compacting equipment will be adjusted as required to obtain the minimum specified density. Evaluations of the construction work will include the following:

- Observations of the water content and other physical properties of the soil during processing, placement and compaction;

- Observations of the thickness of lifts as loosely placed and compacted (max. 6-inch compacted lift or 6 to 9-inch loose lift);
- Observations of the use of proper equipment for the construction and effective use of same to properly prepare materials;
- Observations of the action of the compaction and heavy hauling equipment on the construction surface (sheepsfoot penetration, pumping, cracking, etc.); and
- Observations of the number of passes used to compact each lift and approximate speed of compactor.

Determination of in-place soil moisture and density will be performed in accordance with the following methods:

Test	ASTM Standard No.
- Moisture and density of soil and soil aggregate, in-place, by Nuclear Methods	D2922-81 D3017-78

Malcolm Pirnie will perform field tests to measure the dry density and moisture content of the compacted clay using Troxler nuclear moisture/density gauges Model 3411-B. These measurements will be performed with the gauge in the direct transmission mode with the depth probe typically extended 6 inches. The gauges will be standardized daily. In addition, the calibration of each nuclear densitometer shall be performed a minimum of four (4) times (once prior to the test patch) during each construction season using ASTM D-1556. The QA inspector will program the nuclear densitometer with the maximum dry density of the soil actually being placed (viz. based on material evaluation of stockpile being placed). The construction personnel will not be permitted to proceed with hydraulic conductivity measurements until the in-place soil density is approved by the QA personnel (see Form E, Appendix B).

c. Undisturbed Hydraulic Conductivity (Permeability) Measurements

Undisturbed laboratory permeability measurements will be performed on Shelby-Tube samples of the completed barrier layer. A maximum hydraulic conductivity of 1.0x10-7 cm/sec will be used for determination of acceptability (see Form D, Appendix B).

The test method utilized will be an:

> undisturbed Shelby Tube hydraulic
> conductivity test (saturated
> backpressure triaxial - see Appendix C-2.)

The Shelby tube sample will be obtained from the wedge of soil between the probe and the back of the nuclear densitometer gauge.

d. Thickness Verification

The existing daily/intermediate cover will be stripped of all vegetation, graded to a uniform slope, and compacted prior to placement of the final cover system material. Construction personnel will obtain the approval of the subgrade from Malcolm Pirnie's QA personnel before beginning the final cover system construction.

Following a visual inspection and approval of the subgrade by QA personnel, a licensed land surveyor will perform a topographic survey of the site using a 50' x 50' grid interval over the entire area to be capped. Grade stakes will be used to establish the appropriate subgrade elevations. The survey will be referenced to a horizontal grid system and vertical control on site. The survey will be the determining factor in checking that the subgrade had been graded to the minimum approved elevations. The top of subgrade will be scarified, unless otherwise directed by the QA Engineer, prior to final cover system construction.

The minimum barrier layer thickness of 24 inches will be confirmed by contracting with a licensed land surveyor for the performance of a topographic survey of the site following completion of the barrier layer construction. The licensed land surveyor will utilize the same grid system as the survey completed before final cover system construction. Construction personnel will obtain the approval of the QA Engineer for minimum cap thickness before placement of topsoil.

5.1.3 Topsoil Layer

The topsoil layer is the uppermost component of the cover system. Its functions are to protect the underlying layers from mechanical damage, and (in conjunction with a vegetative cover) to protect against erosion.

Preconstruction inspection activities will include checking topsoil properties against the design specifications and ensuring that deleterious materials are not included. The foundation for the topsoil layer will be the 24-inch barrier layer. The 24-inch barrier layer should be checked to ensure that it has been constructed to meet or exceed the specified design, that any specified penetrations are intact and properly oriented and that the integrity has not been impacted by erosion and/or desiccation cracking.

Following the final grading and compaction of the barrier layer, a topsoil layer will be placed over the barrier cap to a uniform depth of twelve (12) inches. Topsoil will not be placed when it is partially frozen or muddy or on the barrier layer when frozen or covered with ice, snow, or standing water. Construction personnel will use grade stakes to establish the appropriate depth of the topsoil layer. Any penetrations of the barrier layer from the grade stakes will be repaired with bentonite prior to the placement of topsoil. During construction of the topsoil layer, QA inspection personnel will monitor the uniformity of the application process, observe the placement procedure to ensure that the soil is not overly compacted, and measure the thickness and slope of the topsoil layer. QA inspection personnel should also ensure that care is taken in the vicinity of vents, monitoring wells, or other protrusions to prevent damage by construction equipment. A topographic survey will be performed by a licensed land surveyor to verify the thickness of the topsoil layer. He will follow the same procedure as discussed in Section 5.1.2.2.d.

Topsoil placement, preparation for seeding, and the seeding will take place in a more or less continuous operation. The appropriate seed mixture, fertilizer and additives are defined in the project specifications. The application rate of seed, fertilizer and additives will be monitored to confirm that it is as specified in the design and consulting agronomist. QA inspection personnel will verify that all vents and standpipes or any other penetrations through the cover are not damaged by additive application processes.

QA inspection personnel will ensure that the application equipment is appropriate for the job. The rate of seed and mulch application, amount and uniformity of coverage, and watering instructions, will be as specified. Mulch will be applied within 72 hours of seeding and will be uniformly applied in a continuous blanket to reasonably cover the soil from view. Care will be taken not to oversupply mulch. Perimeter areas will be examined to ensure that bare spots are not left inadvertently.

Timing of seeding is important, particularly for grasses. QA inspection personnel will ensure that it occurs during the designated period and that the weather is favorable. (For example, seeding will not take place during high wind or rain or when the soil is frozen.)

Topsoil placed and graded on slopes steeper than five (5) percent (viz. drainage ditch areas) will be promptly stabilized with suitable equipment, fertilized, seeded, and mulched.

5.1.4 Quality Assurance (QA) Testing Frequency

Testing frequencies for each of the QA testing categories identified in Section 5.1.1 have been summarized in Table 2. All QA testing is related to the construction sequence. To facilitate the QA program, the following definitions are presented:

- A layer is defined as a compacted stratum composed of several lifts constructed without construction joints.
- A lift is defined as a constructed segment of a layer composed of soil materials placed in a maximum six (6) inch (6-9 inch loose thickness) compacted thickness.

All quality assurance testing will be conducted in accordance with the project specifications or as specified herein. Where there are discrepancies between the design plans/specifications and QA Plan, it shall be the Contractor's responsibility to bring the discrepancy to the attention of the QA Engineer or Project Manager for written clarification. All applicable testing methods as previously identified will be observed.

TABLE 2

PALMER STREET LANDFILL
FINAL CAP CONSTRUCTION
QUALITY ASSURANCE

TESTING FREQUENCIES

TEST	FREQUENCY
MATERIALS EVALUATION:	
Water Content (ASTM D 2216-80)	1 per 1000 cu. yd.
Gradation Analysis (ASTM D422, D421)	1 per 1000 cu. yd.
Atterberg Limits (ASTM D4318-83)	1 per 1000 cu. yd.
Moisture-Density Relationship (Modified Proctor: ASTM D1557-78)	1 per 5000 cu. yd.
Moisture-Density Relationship (Standard Proctor: ASTM D698-78)	1 per 5000 cu. yd.
Recompacted Permeability (Current Literature: see Appendix C-1)	1 per 5000 cu. yd.
Organic Content (ASTM D2974-87)	Whenever organic soils are visually encountered
CONSTRUCTION QUALITY EVALUATION:	
In-Place Moisture-Density Test (including moisture content) (ASTM D2922-81, D3017-78)	Minimum of 9 per acre per lift of barrier layer placed: For long, thin areas such as ditch sidewalls, a minimum of 3 per section
Undisturbed Shelby-Tube Hydraulic Conductivity (Current Literature: see Appendix C-2)	1 per acre per lift of barrier layer placed

Documentation and reporting of test results will be in accordance with the requirements identified in Section 8.0.

Preconstruction testing as specified in Section 5.1.2 will be conducted on stockpiled material samples obtained from the borrow location. Construction testing will be conducted on samples taken from the material during the course of the work. Barrier layer QA testing will consist of material evaluation tests and construction quality evaluation tests as described in Sections 5.1.2.1 and 5.1.2.2, respectively. The exact location of the construction quality tests will be determined in the field by the QA personnel. The construction personnel will measure to the nearest foot, and mark by staking and reference the location of all construction quality tests to the existing horizontal grid system. The QA testing frequencies are specified on Table 2. Sampling of soil will be in accordance with sampling and testing strategies discussed in Section 6.0.

Additional testing will be utilized at the discretion of the Moench Tanning Co. or Malcolm Pirnie, Inc. when visual observations of construction performance indicate a potential problem.

5.1.5 Barrier Layer Perforations

All barrier layer perforations will be completed in accordance with the testing frequencies identified in the above mentioned sections.

All barrier layer perforations (viz. nuclear density test probe locations, grade stake locations, and Shelby tube sampling locations) will be backfilled with a dry soil-bentonite (50 percent/50 percent) mixture by QA personnel. The mixture will be compacted in place with a tamping rod or hand tamper, depending on the size of the perforation.

5.1.6 Barrier Layer Test Patch

As requested by the NYSDEC, a barrier layer test patch will be constructed either within the soil material borrow area or at the site prior to material placement. The purpose of the test patch will be to determine soil characteristics and suitability of the material for final cover. The

NYSDEC will receive prior written notification indicating the anticipated test patch construction date.

The test patch will occupy an area of approximately 50'x 50' and will be constructed in two six-inch (after compaction) lifts. The same equipment used for placement of the final cover will be used for the patch construction. Prior to placing material, the subgrade will be graded to a uniform slope, will be thoroughly compacted, any existing vegetation removed and the top of it scarified. All work will be observed by the QA Engineer.

The same general QA procedures described in Section 5.1 will be adhered to during the patch construction and testing. More specifically, the following requirements will be met:

- Falling Head Permeability: 1×10^{-7} cm/sec (maximum);
- Laboratory Testing will be performed on a representative sample of the soil to be used in construction of the test patch:
    - o Gradation (sieve and hydrometer)
    - o Atterberg limits
    - o Moisture-Density Relationship (standard and modified Proctor);
- Cover material will be placed in two maximum six-inch (after compaction) lifts, 6 to 9 inch loose lift thickness;
- Cover material will be compacted to greater than 90% of Modified Proctor Density in accordance with the procedures for determining the acceptable level of compaction as described in Appendix D;
- A nuclear densitometer will be used to measure in place moisture content and density once per lift;
- Moisture content to be greater than optimum prior to compaction; and
- Shelby tube laboratory permeability testing once/lift: Shelby tube samples will be obtained in the wedge of soil between the end of the nuclear densitometer gauge probe and the back of the probe.

In addition to the above, the following will be documented:

- uncompacted and compacted lift thickness;
- maximum barrier soil clod size (visual);
- specification for compaction equipment utilized;
- the action of the compaction and heavy hauling equipment on the construction surface (sheepsfoot penetration, speed, etc);
- the average number of passes used to compact each lift; and
- compaction equipment speed.

Results of the barrier layer test patch shall be submitted to the NYSDEC for review and aproval prior to the initiation of barrier soil placement activities.

5.2 SYNTHETIC MATERIALS QUALITY ASSURANCE

5.2.1 General

The surface water control system between Areas 1 and 2 will consist of an 18-inch galvanized metal pipe buried along the line of the existing ditch between Point A and the northwest corner of Area 2. The pipe will transport both off-site and on-site runoff to Cattaraugus Creek.

The recompacted earth barrier will be constructed above the pipe. To ensure that leachate cannot enter the pipe, a 60-mil HDPE synthetic liner will be placed in the trench beneath and around the pipe and will be keyed beneath the earth barrier for an effective seal. Construction methods will comply with the project plans and specifications. Quality assurance procedures regarding the synthetic liner are outlined in the following sections.

5.2.2 Synthetic Liner

The high density polyethylene (HDPE) synthetic liner material (herein after referred to as liner) will be selected for use by the Contractor in accordance with the design plans and specifications. The contract documents define the required quality assurance testing of the liner installation.

5.2.2.1 Material Evaluation

Quality assurance evaluation of the HDPE liner material will begin with the testing of the HDPE resin used to produce the HDPE liner. Prior to shipping the resin to the sheet manufacturer, the following tests will be performed by the resin manufacturer:

- Melt index
- Density

All incoming raw materials will be sampled by the sheet manufacturer to ensure compliance with the requirements for the liner, and to further verify the resin quality. All properties determined in these tests shall be completed in the final sheet certificate from the liner manufacturer and included in the construction monitoring report.

The liner material proposed will be manufactured in accordance with the American Society for Testing Materials standards stated in the specifications and so certified, by affidavit, from the liner manufacturer to the installation contractor. This affidavit will be included in the construction monitoring report provided by Malcolm Pirnie, Inc.

Upon delivery at the site, the Manufacturer or Installation Contractor and the QA inspector will conduct a surface inspection of all rolls or blankets for defects and for damage. This inspection will be conducted without unrolling rolls or unfolding blankets unless defects or damages are found or suspected. The QA Engineer will note all:

- rolls or blankets, or portions thereof, which should be rejected and removed from the site because they have severe flaws; and
- rolls or blankets which include minor repairable flaws.

The liner will be stored under the responsibility of the Manufacturer or Installation Contractor. The area designated for storage of the liner will be protected from ultraviolet light exposure, precipitation or other inundation, theft, vandalism, mud, dirt, dust, puncture, cutting or other damaging or deleterious conditions. The QA Engineer will verify that storage of the liner ensures adequate protection.

The surface to be lined will be compacted to minimum 90% of maximum density as determined by Modified Proctor (ASTM D1557-78), and will be free from stones, sticks, roots, sharp objects, holes and discontinuities in grade. Synthetic liner installation will not commence until the QA Engineer approves the subgrade surface and installation conditions. The liner will be protected on both sides through the use of a geotextile fabric.

5.2.2.2 Construction Quality Evaluation

The quality assurance of the liner installation will be divided into the following segments:

- Visual Inspection
- Destructive Material Testing
- Non-Destructive Testing

A panel is the unit area of liner to be seamed in the field. It can be either an entire roll or a portion of roll cut in the field.

Each panel will be given an "identification code" (number or letter-number) consistent with the layout plan. This identification code will be agreed upon by the QA Engineer and Manufacturer or Installation Contractor. This identification code will be as simple and logical as possible. (Note that roll numbers and blanket numbers established in the manufacturing plant and fabrication factory are usually cumbersome and are not related to location in the field.)

The Manufacturer or Installation Contractor will establish a table or chart showing correspondence between roll numbers/blanket numbers and identification codes. The panel identification code will be used for all quality assurance records.

The Manufacturer will verify that the liner thickness is in conformance with the specifications. Thickness readings will be taken during manufacturing at appropriate intervals across the panel width and periodically along the panel length. Readings will be taken across the width at any point where the panel has been cut.

The QA inspector will record on this daily report the panel identification and panel location and date installation of each panel.

a. Visual Inspection

The liner manufacturer or installation contractor will document in writing that the surface on which the liner will be installed is acceptable. This documentation will be given to the QA Engineer prior to commencement of the liner installation.

A visual inspection will be conducted by the QA personnel of each panel as it is being placed. This is necessary to ensure that the liner material is free from transport and unloading damage, pinholes, pores or other detrimental defects. The QA personnel will mark each defect for future Contractor repair. The amount of liner unrolled will be limited to the amount of liner that can be properly seamed during a given day. As the liner is being unrolled, the edge of each sheet will be ballasted with sand bags. Field seams will be made by overlapping adjacent sheets a minimum of six (6) inches. QA personnel will spot check overlap and cleanliness of adjacent sheets prior to beginning of the weld.

Prior to beginning an extrusion weld, the Contractor will clean the surfaces to be welded. No welding will take place when the ambient air temperature is below 45°F or above 90°F. The air temperature will be monitored by the QA personnel and the Manufacturer or Installation Contractor.

b. Destructive Material Testing

There are two types of destructive tests to be used by the liner installer to determine the strength of a liner seam:

- peel
- shear

Destructive peel and shear tests will be conducted in the field on samples selected randomly by the QA inspector during each welding day. For each test, a representative sample will be cut into one inch wide strips vertically across the weld and inserted into a tensile testing machine.

For peel testing, one end of the test strip and the closest edge of the adjacent piece are clamped and pulled, placing the seam in tension (ASTM D3083). In shear testing, a sample weld is clamped and then pulled apart, placing the seam in shear (ASTM D413).

Test seams will be made on fragment pieces of liner to verify that seaming conditions are adequate. Such test seams will be made at the beginning of each seaming period, at the Engineer's discretion, and at least once each four hours, for each seaming apparatus used that day. Also, each seamer will make at least one test seam each day.

The test seam sample will be at least 2 feet long by 1 foot wide with the seam centered lengthwise. Two adjoining specimens a minimum of 1 inch wide each will be cut from the test seam sample by the Manufacturer or Installation Contractor. These specimens will be tested in the field by hand or tensiometer, and will not fail in the seam. If a test seam fails, the entire operation will be repeated. If the additional test seam fails, the seaming apparatus or seamer will not be accepted and will not be used for seaming until the deficiencies are corrected and two consecutive successful full test seams are achieved.

The QA inspector will observe all test seam procedures. The remainder of the successful test seam sample will be assigned a number and marked accordingly by the QA inspector and Manufacturer or Installation Contractor, who will also log the date, hour, ambient temperature, number of seaming unit, name of seamer, and pass or fail description. The seam itself will be retained in the OWNER's archives.

Destructive test samples will be packaged and shipped under the responsibility of the Manufacturer or Installation Contractor in a manner which will not damage the test sample. The QA inspector will verify that packaging and shipping conditions are acceptable. The QA inspector will be responsible for packaging and storing the archive samples.

The QA personnel will review independent laboratory test results as soon as they become available.

All test results from the Manufacturer's or Installation Contractor's laboratory will be submitted to the QA Engineer as soon as they become available.

One sample weld per day will be sent to a laboratory to determine the bonded seam strength. The results will be included in the construction monitoring report.

c. Non-Destructive Testing

The following test will be performed along the entire length of all field seams and any repair seams. The purpose of this test is to check the continuity/water tightness of seams. It does not provide any information on seam strength. Testing will be done as the seaming work progresses, not at the completion of all field seams.

1) Vacuum Testing is a non-destructive test to locate any possible leak in the weld by using soapy solution and a clear-view glass top suction chamber attached to a vacuum pump. The procedure is as follows:

   a) Thoroughly soap (one oz. soap to one gallon water) a seam section and center the suction chamber, typically 3 feet long, over the seam. The rubber gasket on the bottom of the chamber must fit snug against the liner. As 3-5 inches of vacuum is drawn, the chamber will automatically seal itself to the liner.

   b) As proper vacuum is achieved, soap bubbles will appear in any unbonded areas. Dwell time is usually 10-15 seconds per seam section.

   c) Should a pinhole or unbonded section be discovered, the questionable area will be properly marked for future repair, and retested.

   Should it not be feasible to vacuum test a seam, ultrasonic testing will be utilized as the alternate non-destructive test method.

2) Ultrasonic (High Frequency) Pulse Echo Testing is done by the liner installer to test seam soundness by passing a high frequency sound wave through the seam overlap to detect discontinuities in the welded seam which may not be visible. Again any discontinuity will be marked, documented, repaired and retested.

6.0 SOIL SAMPLING AND TESTING STRATEGIES

6.1 STOCKPILED SOIL SAMPLING METHOD

As shown in Figure 3, twelve samples of approximate equal volume will be collected from the top, middle and bottom of each 1000 cu. yd. stockpile (as discussed in Section 5.1.2.1) by QA personnel. The samples will be composited to give one representative aliquot per 1,000 cubic yards for soil laboratory analysis. Each sample will be collected using a shovel.

6.1.1 Sampling Procedure

Step 1: Using the shovel, penetrate the pile to a depth of about two to three feet.

Step 2: Place the shovel into the hole and collect a sample.

Step 3: Transfer the sample to a specially prepared mixing area.

Step 4: Repeat steps 1 through 3 at each of the sampling points (see Figure 3).

Step 5: Mix subsamples using shovel into one homogenous mass and place in a properly labeled container.

Step 6: Attach label to container and record in field log book.

Step 7: Return remaining contents of composite sample to stockpile.

Step 8: Deliver the composited sample aliquots to the laboratory for analysis as soon as possible.

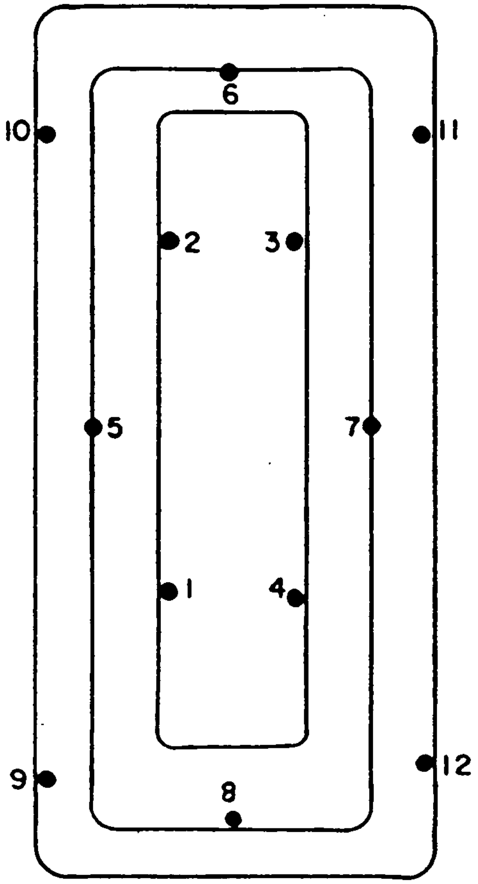
6.1.2 Sample Containers

Plastic 5-gallon buckets (filled completely) will be used to transport soil samples to the laboratory for analysis.

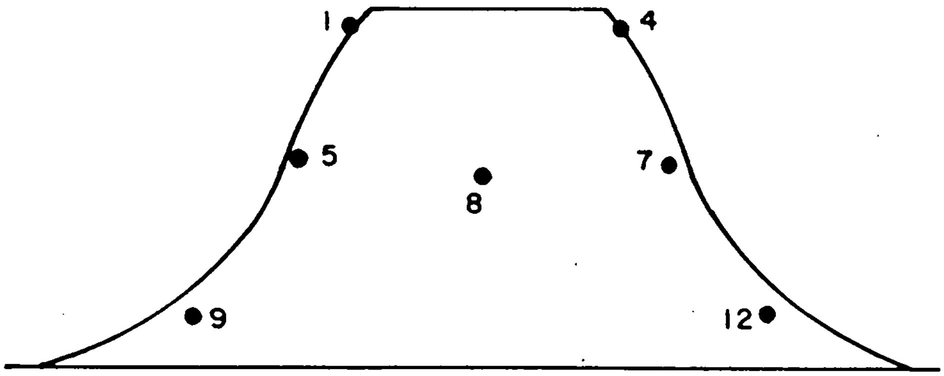
6.1.3 Sample Identification

All samples will be identified with chain-of-custody labels which will include the following information:

- Moench Tanning Co., Palmer Street Landfill Cap;
- Sample number;



PLAN



SECTION

MOENCH TANNING COMPANY
PALMER STREET LANDFILL

QA SAMPLING PROCEDURES DIAGRAM

MALCOLM PIRNIE

- Initials of QA inspector or sample collection personnel;
- Date of collection; and
- Location of collection (i.e., stockpile number and/or location).

6.1.4 Field Log Book

All information pertinent to each sampling event will be recorded in a field log book by QA personnel. The log book will be bound with consecutively numbered pages. Each page of the log book will correspond to a stockpile and will contain the following information:

- Sample number;
- Approximate location of stockpile;
- Number of stockpile;
- Field observations;
- Climatologic conditions; and
- Date of collection.

The log book will be maintained in safe storage between sampling events.

6.2 COMPOSITE SOIL SAMPLING METHOD (for Materials Evaluation)

The sample to be used for laboratory tests run on every 5,000 cu. yd. of material will be a composite of sample aliquots (collected by field personnel in accordance with Section 6.1) of five (5) 1,000 cu. yd. stockpiles. The samples will be composited in the lab. The composite samples representing 5,000 cu. yd. of soil will then be thoroughly mixed and quartered with one (1) quarter being used as the representative sample for testing.

6.3 IN-PLACE MOISTURE-DENSITY TESTS

The frequency of moisture-density testing is discussed in Section 5.1.4 Quality Assurance (QA) Testing Frequency. These tests will be spaced at approximately 70-foot intervals. These intervals will be taped off in the field by QA personnel. The QA inspector may determine that more than the minimum (i.e., nine) required moisture-density tests per acre are necessary to accurately evaluate the quality of the compacted soil lift being evaluated. Any additional tests deemed necessary will be located at the QA inspector's discretion and tied into the grid system as discussed in Section 5.1.4.

Testing of consecutive lifts will be offset laterally and axially (approximately 35 feet forward and 35 feet to the side) from the prior lift's tests. This will help to eliminate "stacking" of moisture-density tests.

6.4 UNDISTURBED HYDRAULIC CONDUCTIVITY TESTS

The frequency of undisturbed hydraulic conductivity testing is discussed in Section 5.1.4. Undisturbed Shelby-Tube samples will be spaced at approximately 105-foot intervals. These intervals will be taped off in the field by the QA personnel. Testing of consecutive lifts will be offset both laterally and axially by no less than 100 feet.

6.5 TREATMENT OF LABORATORY TEST RESULT OUTLIERS

Occasionally, one laboratory test value deviates markedly from the remainder of the test values. Such a value is called an outlier. When an outlier is determined to exist, the following procedures will be followed by laboratory personnel:

- Recalculate the test value checking for math errors;
- Check any values used for comparison, making sure they were the correct values to be used;
- If outlier value(s) still exists, perform test again on the same soil sample;

- If outlier value(s) still exists, discuss value(s) and course of action with QA Engineer.

7.0 CORRECTIVE MEASURES

When material or work is rejected because field observations or tests indicate that it does not meet the design specifications, corrective measures must be implemented. For material or workmanship in question because of QA inspection personnel observations or test results, additional testing may be necessary. The following are procedures and corrective measures to be followed for QA testing problems which are likely to occur:

- <u>Excessive Drying or Wetting of Stockpiled Soil</u> - If excessive drying or wetting of stockpiled soil becomes a problem, consideration will be given to cover the piles with plastic sheets to minimize moisture loss or gain until the material is utilized in the construction activities.

- <u>In-Place Moisture-Density Test Failures</u>

  o <u>Moisture</u> - When the moisture content is determined to be too far below optimum, the compacted soil will be disked and moisture added to achieve a moisture content of greater than optimum prior to recompaction. When the moisture content is so high that the soil cannot be compacted to required density limits, the soil will be disked or scarified and left to dry in the sun and wind prior to recompaction. If this action does not result in sufficient drying, the soil will be removed and stockpiled until it dries to an acceptable moisture content. Under either failure condition, the extent of work will include the area delineated by a circle with the center at the location of the failed test and a radius corresponding to the distance from the location of the failed test to the nearest passing test or to a closer passing test as determined by additional testing. Retesting will be performed within 10 feet of the original location as the failed test after corrective measures have been taken.

  o <u>Density</u> - When the compaction is less than 90% of the maximum dry density or is not considered acceptable using the procedures described in Appendix D, the lift of soil in the work area shall be deemed unacceptable. The soil will be removed and set aside for alternative uses. The extent of the work area will include the area delineated by a circle with a center at the failed test and a radius of 50 feet.

- <u>Erosion and/or Desiccation Cracking of Completed and Compacted Soil Layers, Lift or Subgrades</u> - Dry weather and/or high wind conditions may lead to erosion and/or desiccation cracking of completed and compacted soil layers, lifts or subgrades. When erosion and/or desiccation cracking occurs, the affected area will be scarified, wetted, and recompacted prior to replacement of new soil. The new soil will be placed, compacted and tested in accordance with Section 5.0. Consideration will be given to the use of plastic sheets to limit erosion and desiccation cracking if the problem occurs on a routine basis.

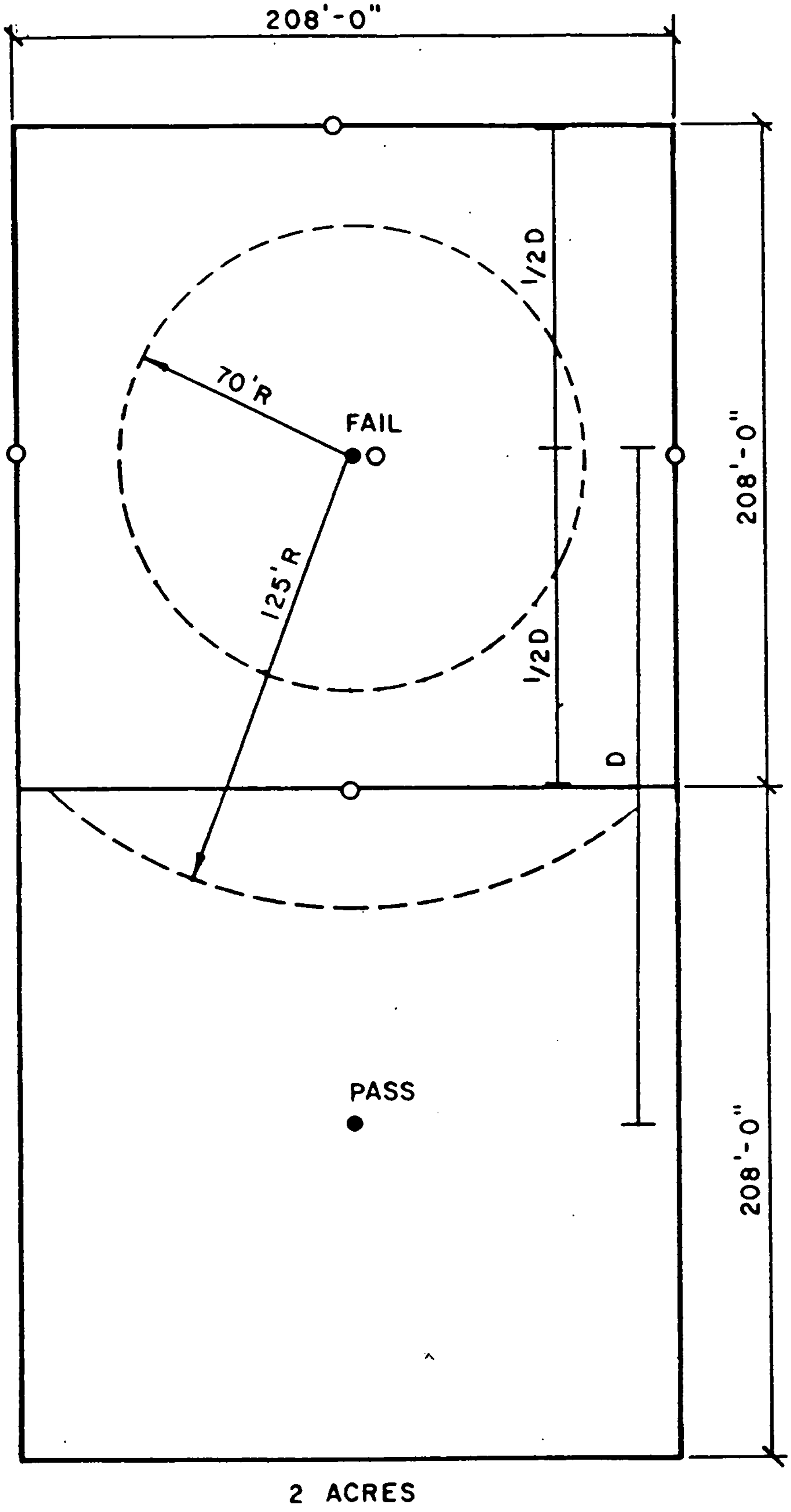
- <u>Ponding of Water on Completed Compacted Soil Layers, Lifts or Subgrades</u> - If ponding of water on completed, compacted soil layers, lifts or subgrades become a routine problem, the completed surfaces which are to receive additional lifts of compacted soil will be rolled with a smooth drum roller at the end of each day. This will limit ponding as well as help to minimize drying and desiccation cracking. If the smooth drum roller is used, the affected area will be scarified prior to placement of the next lift of soil.

- <u>Hydraulic Conductivity Test Failure</u> - The minimum acceptable values and testing standards are discussed in Section 5.1.2.2.c. If a test during materials evaluation fails (viz. greater than 1.0×10^{-7} cm/sec), the test will be repeated. If the test fails a second time, the material will be rejected for use as barrier layer material.

  If the Shelby-Tube hydraulic conductivity test fails, four (4) supplemental Shelby-Tube measurements will be taken approximately 100 feet from the failed test location (see Figure 4). The results of the supplemental tests will be used in conjunction with the original test to establish the extent of the work area where the lift of soil will be removed and stockpiled for alternative uses prior to placement, compaction and testing of the next lift of soil. The extent of the work area will include those areas delineated by circles with midpoints at the failed test locations and a radius of 70 feet Once corrective measures have been applied, retesting will be performed within ten feet of the location of the original failed test.

  In lieu of supplemental permeability testing, the CONTRACTOR will have the option of immediately removing and stockpiling (for alternative uses) the entire acre-lift of soil followed by placement, compaction and testing of a new lift of soil. The acre-lift of soil will be defined as a circle with a center at the failed test and a radius of 125 feet.

FIGURE 4



LEGEND

● ORIGINAL TEST LOCATION

○ ADDITIONAL TEST LOCATION

D APPROXIMATELY 210' OR DISTANCE BETWEEN 2 ADJACENT ORIGINAL TESTS AS PLACED IN THE FIELD BY QA/QC INSPECTOR.

MOENCH TANNING COMPANY
PALMER STREET LANDFILL

TESTING STRATEGIES FOR HYDRAULIC CONDUCTIVITY TESTS

MALCOLM PIRNIE

Observations and test results which indicate adverse conditions not corrected by the CONTRACTOR, should be well documented and discussed with the project engineer before specifying corrective measures to Moench Tanning Co. The general procedure for handling QA problems or differences (not specifically discussed above) is specified in Section 3.2.3.

8.0 DOCUMENTATION

8.1 GENERAL

Malcolm Pirnie, Inc. will document all activities associated with the construction of the landfill cap. Such documentation will include, at a minimum, daily reports of construction activities, photographs and sketches, as necessary. Field investigation reports will be filled out by the QA Engineer or specialty inspectors when those people visit the site (see Form F, Appendix B).

8.2 CONSTRUCTION MONITORING

Construction of the landfill cover system and appurtenant items will be monitored by Malcolm Pirnie, Inc. QA personnel.

8.2.1 Daily Inspection Reports

Standard daily reporting procedures will include preparation of a summary report with supporting data sheets and, when appropriate, problem identification and corrective measures reports (see Form G of Appendix B for Daily Report).

A report will be prepared and submitted to the QA engineer daily by on-site QA personnel. These reports will provide the chronologic framework for identifying and recording all other reports. Additional information which may be included on the forms by the QA personnel includes:

- Unit processes, and locations, of construction under way during the time frame of the daily inspection report;
- Equipment and personnel working in the area including subcontractors;
- Descriptions of areas being inspected and documented; and

- Description of offsite materials received, including any quality verification (vendor certification) documentation.

8.2.2 Data Sheets

All field and/or laboratory tests will be recorded on data sheets. The following data sheets will be utilized:

- Laboratory Testing Summary Report
- Grain Size Distribution Test Report
- Proctor Test Report
- Permeability Test Results (Undisturbed Shelby-Tube and Recompacted)
- Nuclear Density Test Data
- In-Situ Permeability Test Report

The completed reports and data sheets will be available on-site and will be submitted to the NYSDEC on a weekly basis and will also be submitted as part of the final Construction Monitoring Report.

8.2.3 Problem Identification and Corrective Measures Reports

A problem identification report (see Form H, Appendix B) and a corrective measure report (see Form I, Appendix B) will be completed whenever field problems are encountered and corrective measures may be necessary. These reports will be attached to the associated daily reports.

The NYSDEC will be notified (by telephone) of problems requiring modifications to design plans and details prior to proceeding or completion of the construction item. Changes or additions will be noted in constructing record drawings. Changes to previously submitted data or reports will be noted accordingly and submitted with the following weekly report.

8.2.4 Acceptance of Completed Components

All daily reports, data sheets, problem identification and corrective measures reports will be reviewed by the QA Engineer. The documentation will be evaluated and analyzed for internal consistency and for consistency with similar work. Timely review of these documents will permit errors, inconsistencies, and other problems to be detected and corrected as they occur.

The above information will be assembled and summarized as part of the final Construction Monitoring Report. The report will indicate that the materials and construction processes comply with the closure plans and specifications for this project.

8.3 WEEKLY CONSTRUCTION MONITORING REPORTS

Weekly construction monitoring reports will be submitted to the NYSDEC. These reports will include a presentation of all installation practices and quality assurance testing (with discussion, as appropriate) including:

- soils testing data (field and laboratory);
- barrier layer placement and compaction;
- topsoil placement;
- seeding;
- fertilizing and mulching;
- miscellaneous equipment (e.g. infiltrometers) installation; and
- updates of the project schedule, as necessary.

8.4 FINAL CONSTRUCTION MONITORING REPORT

Malcolm Pirnie, Inc. will prepare a final construction monitoring report addressing each item identified above for construction for the final cover system at the Palmer Street Landfill. The report will include an analysis of the contractors compliance with the project closure plans and specifications and a summary of QA sampling and testing. The report will also include:

- Scale drawing depicting final subgrade elevations, final cap elevations, and final topsoil elevations.

- Scale drawings depicting the location of the construction and QA testing; (each soil lift will have its own plan sheet).
- Statements pertaining to the extent of construction, i.e., depths, plan dimensions, elevations and thickness.
- A discussion of any remedial actions which were necessary. This will include a description of the overall circumstances, actions taken and results of retesting;
- Malcolm Pirnie, Inc. QA personnel information;
- Barrier soil evaluation data and summary; and
- Weekly construction monitoring reports (viz. compilation of daily activity reports and data sheets).

The summary technical report will provide an evaluation of the construction project and all of the pertinent testing. The report will certify the results of the various field tests and laboratory permeability tests performed and assess whether or not the constructed project is in compliance with the closure plans and specifications.

8.5 CERTIFICATION OF CLOSURE CONSTRUCTION

Upon completion of closure construction activities, Moench Tanning Company and Malcolm Pirnie, Inc. shall submit, in conjunction with the Final Construction Monitoring Report, to the Commissioner certification that the Palmer Street Landfill has been closed in accordance with the specifications, requirements and NYSDEC approved modifications (if any) and is fully capable of being maintained in accordance with the specifications and requirements of the Post-Closure Plan.

8.6 STORAGE OF RECORDS

During the construction of the final cover system at Palmer Street Landfill facility, the QA Engineer will be responsible for all facility QA documents. This includes the QA Engineer's copy of the design criteria, closure plans, and specifications, the QA Plan, and the originals of all data sheets and reports. All originals will be maintained in the QA

Engineer's office. Duplicate records will be kept in the field office to avoid loss of this information if the originals are destroyed.

Once the facility construction is complete, the document originals will be stored by Moench Tanning Co. in a manner that allows for easy access while still protecting them from any damage. An additional copy will also be kept at the landfill facility if this is in a different location from Moench Tanning's files. A final construction monitoring report will be kept by the NYSDEC in a publicly acknowledged repository. All documentation will be maintained through the operating and post-closure monitoring periods of the landfill facility.

APPENDIX A

CONSTRUCTION SCHEDULE

MOENCH TANNING COMPANY
PALMER STREET LANDFILL

CLOSURE CONSTRUCTION SCHEDULE(1)(2)

MILESTONE	ESTIMATED NUMBER OF MONTHS TO ACCOMPLISH MILESTONE
Regulatory Approval of Closure/ Post Closure Plan	-
Preparation of Bid Documents/ Specifications	2
Solicit Bids	2
Selection of Contractor	1
Execute Contract	1
Closure of Landfill Areas 2 & 3	7
Closure of Landfill Area 1/ Complete Construction	7
TOTAL	20

NOTES:

1. Schedule assumes that no work will be performed between November 30 and April 1.
2. Schedule assumes two full construction seasons.

APPENDIX B

STANDARD DOCUMENT SHEETS

MALCOLM PIRNIE, INC.

Project.........
Project Number..
Location........

Sample Number	Moisture Content %	Gravel %	Sand %	Silt %	Clay %	Classification
P 11	12.0	32.6	20.1	31.6	15.7	GC
P 12	10.4	31.4	22.3	24.5	21.8	GC
P 13	10.2	29.3	22.6	25.4	22.7	GC
P 14	11.3	27.6	22.7	35.0	14.7	GC
P 15	11.4	27.3	22.4	35.0	15.3	CL
P 16	11.0	26.8	22.4	32.7	18.1	CL
P 17	9.6	28.8	23.8	30.3	17.1	GC
P 18	10.0	30.4	22.8	31.3	15.5	GC
P 19	11.1	26.5	23.4	27.7	22.4	CL
P 20	11.4	25.1	22.5	36.3	16.1	CL

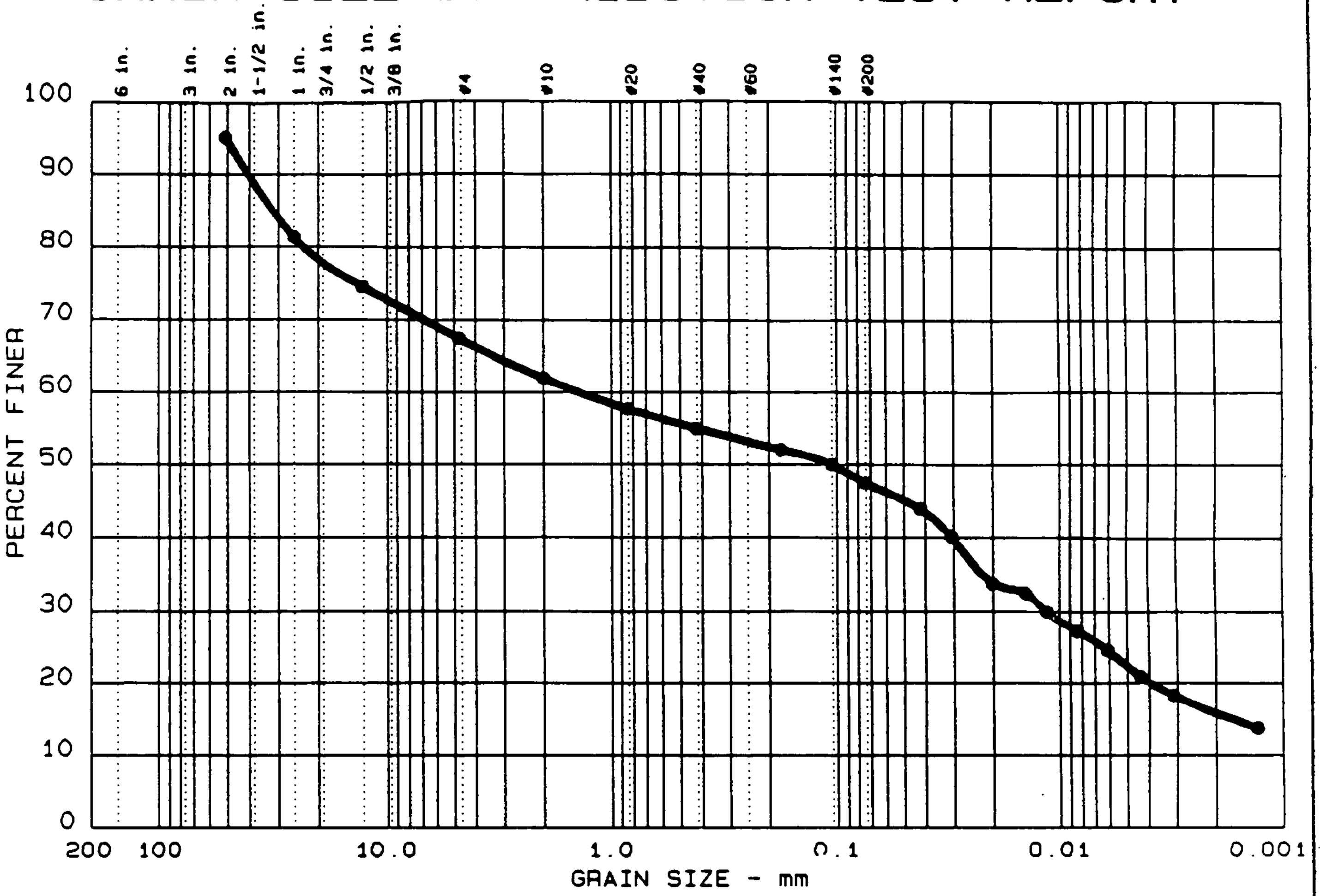
MALCOLM PIRNIE, INC.

Project.........
Project Number..
Location........

Sample Number	Liquid Limit %	Plasticity Index	Optimum Moisture Content %	Maximum Dry Density pcf	Permeability cm/sec
COMP 4	28.8	8.7	10.4	132.1	5.3 E -9
COMP 5	28.5	9.3	10.7	134.7	1.0 E -8

FORM B

GRAIN SIZE DISTRIBUTION TEST REPORT



	Test	% +3"	% GRAVEL	% SAND	% SILT	% CLAY
●	1	0.0	32.6	20.1	31.6	15.7

	LL	PI	D_{85}	D_{60}	D_{50}	D_{30}	D_{15}	D_{10}	C_c	C_u
●	28.8%	8.7	31.62	1.41	0.11	0.011	0.0017			

MATERIAL DESCRIPTION	USCS	AASHTO
● BROWN, GRAVELLY, SILTY	GC	-

Project No.:
Project:
● Location:

Date:

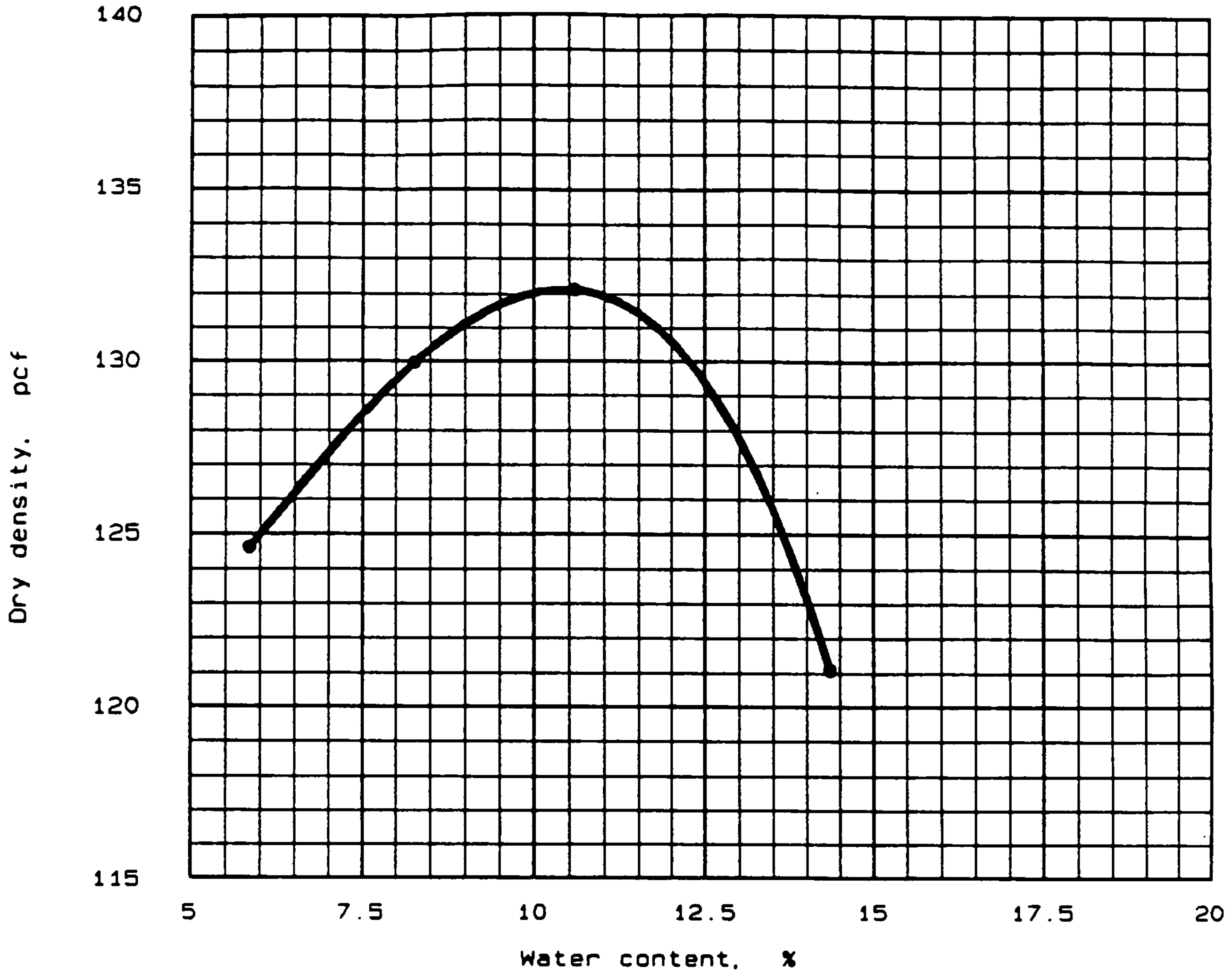
Remarks:
-
-
-
-

GRAIN SIZE DISTRIBUTION TEST REPORT

MALCOLM PIRNIE, INC.

Figure No. -

PROCTOR TEST REPORT



"Modified" Proctor, ASTM D 1557, Method C

Elev/ Depth	Classification		Nat. Moist.	Sp.G.	LL	PI	% > No.4	% < No.200
	USCS	AASHTO						
				2.65			%	%

TEST RESULTS	MATERIAL DESCRIPTION
Optimum moisture = 10.4 % Maximum dry density = 132.1 pcf	YELLOW BROWN, VERY ROCKY

Project No.:
Project:
Location:

Date:

Remarks:

PROCTOR TEST REPORT

MALCOLM PIRNIE, INC.

Figure No.

LCOLM PIRNIE, INC.

Project.........
Project Number..
Location........

PERMEABILITY TEST RESULTS

SAMPLE PARAMETERS	INITIAL	FINAL
Height..................(in)	2.75	2.75
Diameter................(in)	2.875	2.875
Wet Density.............(pcf)	142.73	148.39
Moisture Content..........(%)	11.0	11.4
Optimum Moisture Content..(%)	-	-
Dry Density.............(pcf)	128.6	133.2
Percent Compaction........(%)	-	-
Saturation................(%)		

TEST PARAMETERS	
Test Type.............	UNDISTURBED CONSTANT HEAD
Head Pressure.....(psi)	9
Back Pressure.....(psi)	6
Chamber Pressure..(psi)	11
Fluid.................	DEAIRED WATER
Permeation Time..(days)	8

TEST RESULTS	
Coefficient of Permeability, K..(cm/sec)	1.2 E -7

FORM D

FORM E

NUCLEAR DENSITOMETER DATA SHEET

Project: ______________________ Date: ____________

Client: ______________________ Job No. ____________

Contractor: ______________ Type of Material: ______________

Proctor Test Data - Maximum Density: __________ Optimum Moisture Content: __________

NUCLEAR GAGE
STANDARD COUNTS Density: ______________ Moisture: ______________

TEST NUMBER												
DEPTH OR ELEVATION												
DENSITY COUNT												
WET DENSITY (pcf)												
MOISTURE CONTENT												
MOISTURE (pcf)												
DRY DENSITY (pcf)												
PERCENT MOISTURE												
PERCENT COMPACTION												
PASS (P) OR FAIL (F)												

TEST NO.	LOCATION OR REMARKS

INSPECTION TIME: ______________

INSPECTOR: ______________

DATA CHECKED BY: ______________

TROXLER SERIAL NUMBER: ______________

MALCOLM PIRNIE

FIELD INVESTIGATION REPORT
FORM F

DATE ______________________

DAY

S	M	T	W	TH	F	S

Project Name ______________________ Job No. ____________

Contractor ______________________________________

Subject ______________________________________

____

WEATHER	Brite Sun	Clear	Overcast	Rain	Snow
TEMP.	To 32	32-50	50-70	70-85	85 up
WIND	Still	Moder	High	Report No	
HUMIDITY	Dry	Moder	Humid		

DISTRIBUTION:
1. Proj. Mgr.
2. Field Office
3. File
4. Owner

Signature ______________________ Title ____________

Wiley-Fisk Form 8-3

MALCOLM PIRNIE

FORM G

DAILY REPORT

PROJECT NAME:
JOB NO:
CONTRACT NO.:
CONTRACTOR:
ADDRESS:
TELEPHONE:

LOCATION ______ FROM ______ TO ______ (STA. TO STA
WEATHER ______ TEMP. ______ A.M. ______ P.M. ______ DATE ______

CONTRACTORS WORK FORCE AND EQUIPMENT

Field Engineer				EQUIPMENT		Front Loader	
Superintendent		Iron Worker		Generator		Bulldozer	
				Pumps		Tandem Trucks	
Laborer-Foreman		Carpenter		Welding Equip.			
Laborer						Backhoe	
Operating Engineer		Concrete Finisher		Cherry Picker Ton			
				Tunnel Machine			
				Grade-All			
				Paving Equip. & Roller			
				Air Compressor			

SEE REVERSE SIDE FOR SKETCH YES ☐ NO ☐ ______

WORK PERFORMED: ______

PAY ITEMS:

CONTRACT		STA.		DESCRIPTION	QUANTITY	REMARKS
NO.	ITEM	FROM	TO			

TESTS PERFORMED: ______

PICTURES TAKEN: ______

VISITORS: ______

QA Personnel
Signature ______
Job No: ______
Report No: ______
Sheet 1 of 2

MEETINGS HELD & RESULTS:

REMARKS:

REFERENCES TO OTHER FORMS:

SKETCHES:

SAMPLE LOG

SAMPLE NUMBER:

PPROXIMATE LOCATION OF STOCKPILE:

NUMBER OF STOCKPILE:

ATE OF COLLECTION:

IMATOLOGIC CONDITIONS:

FIELD OBSERVATIONS:

SHEETS: 2 OF 2

PROBLEM IDENTIFICATION REPORT

FORM H

DATE ______________________

DAY	S	M	T	W	TH	F	S

Project ______________________ Job No.__________

Contractor ______________________

Subject ______________________

WEATHER	Brite Sun	Clear	Overcast	Rain	Snow
TEMP.	To 32	32-50	50-70	70-85	85 up
WIND	Still	Moder	High	Report No	
HUMIDITY	Dry	Moder	Humid		

PROBLEM DESCRIPTION (Reference Daily Report No.): ______________________

PROBLEM LOCATION - REFERENCE TEST RESULTS AND LOCATION (Note: Use sketches on back of form as appropriate): ______________________

PROBABLE CAUSES: ______________________

SUGGESTED CORRECTIVE MEASURES: ______________________

APPROVALS:

QA ENGINEER: ______________________

PROJECT MANAGER: ______________________

DISTRIBUTION:
1. Proj. Mgr.
2. Field Office
3. File
4. Owner

QA Personnel
Signature ______________________

Wiley-Fisk Form 8-3

CORRECTIVE MEASURES REPORT

FORM I

DATE ____________________

DAY	S	M	T	W	TH	F	S

Project ______________________________ Job No.__________

Contractor ______________________________

Subject ______________________________

WEATHER	Brite Sun	Clear	Overcast	Rain	Snow
TEMP.	To 32	32-50	50-70	70-85	85 up
WIND	Still	Moder.	High	Report No.	
HUMIDITY	Dry	Moder.	Humid		

CORRECTIVE MEASURES UNDERTAKEN (Reference Problem Identification Report No.): __________

RETESTING LOCATION: ______________________________

SUGGESTED METHOD OF MINIMIZING RE-OCCURRENCE: ______________________________

APPROVALS:

QA ENGINEER: ______________________________

PROJECT MANAGER: ______________________________

DISTRIBUTION:
1. Proj. Mgr.
2. Field Office
3. File
4. Owner

QA Personnel Signature ____________________

Wiley-Fisk Form 8-3

APPENDIX C-1

TEST METHOD FOR RECOMPACTED HYDRAULIC CONDUCTIVITY (PERMEABILITY) TEST

LABORATORY TESTING PROCEDURES

RECOMPACTED PERMEABILITY

A. EQUIPMENT

Compaction Mold (4" or 6")
Recompacted Permeameter Chamber (4" or 6")
Proctor Hammer (5.5 lbs. or 10 lbs.)
20-Kg Balance
Soil Mixer
Graduated Cylinder
Tap Water
High Pressure Permeameter

B. PREPARATION

This procedure requires that the Proctor Test be performed on the soil prior to this test, so that the optimum moisture content and maximum dry denisty of the soil are knowsn.

To perform this test, the soil must be compacted exactly as it was for the Proctor Test (i.e. Standard or Modified test, Method A, B, C or D). The soil must achieve 95% of maximum dry density as determined by the standard test, or 90% of maximum dry density as determined by the modified test. Compaction must be performed on the wet side of optimum.

The procedures and equipment used to determine the permeability of soils compacted by method A (the 4" mold) are differenct than those used for samples compacted by methods B, C or D (the 6" mold). Each are described separately in the Procedure section.

C. PROCEDURE

Initial:

1. From performing the Proctor test, the amount of soil required to fill one mold when compacted should be known. Add enough water to the sample to raise its water content to optimum if the sample were oven dry. Since it is only air dry, and has some residual moisture, it will now be slightly wetter than optimum, which is the desired moisture content for this test. Cover the sample and set aside overnight to cure. Resume the procedure the following morning.

LABORATORY TESTING PROCEDURES

METHOD B, C, D

2. The compaction mold used for this recompacted permeability test is not the same as the one used for the Proctor test. It is approximately 2-1/2 inches deeper. Weigh this mold without the base or collar, and record.

   Though the mold is deeper, the soil must be compacted exactly as was done in the Proctor test. THE SOIL SHOULD STILL BE COMPACTED TO 4.6 INCHES DEEP, as was done originally. The same number of layers and blows per layer, as well as the same amount of soil, must be used. Compact the soil in the permeameter mold on the normal Proctor test base. Do not compact on the permeameter base. The collar need not be used, due to the depth of the mold. The collar will be used, however, in the permeameter set up.

   If the depth of the soil in the mold is significantly different from 4.6 inches, measure down from the top of the mold (without the collar) at 4 evenly spaced points around the perimeter, and average those lengths. Subtract that average from 7 inches, the depth of the mold. Record the length of the sample on the data sheet ("length of sample in 6" mold").

METHOD A

   Weigh a 4-inch compaction mold without the base or collar and record. Assemble the mold, base and collar. Use the regular compaction base - do not compact on the permeameter base. Compact the soil into the mold exactly as was done in the proctor test.

3. Remove the mold, with the soil, from the base. Weigh and record the weight of the mold with the soil in it.

4. Take two moisture content samples from the remaining uncompacted soil. Record the weight of the cans (Wt) and the weights of the

cans with the moist soil in them (Wwt) and set the samples in the oven to dry overnight.

5. Assembling the Permeameter:

In assembling the permeameter, it is crucial that the o-rings be clean and properly seated in order to avoid leaks. If they are carefully placed, only the proper one will fit any given location and they will lie flat without stretching or buckling.

METHOD B,C,D

Place one of the o-rings on the porous stone in the permeameter base. Carefully place the bottom of the mold onto the o-ring in such a way that the flanges on the mold can slide around the threaded rods. Tighten the wing nuts lightly down onto the flanges.

Attach the collar to the mold, using the two remaining slender o-rings to seal: one on the outside and one on the inside of the mold. Lightly tighten down the wing nuts on the collar flanges.

Place the second porous stone onto the soil in the mold. Place the spring on top of the stone; it may not reach above the top of the collar.

Slide the top of the permeameter onto the threaded rods and down onto the top of the collar. Use the last o-ring (the "fattest" one) to seal. Check to see that all the o-rings are properly seated before tightening down the wing nuts.

METHOD A

Place one of the two O-rings on the porous stone in the permeameter base. Carefully place the bottom of the mold onto the O-ring in such a way that the flanges on the mold can slide around the threaded rods. Tighten the wing nuts lightly down onto the flanges. Place the second O-ring on top of the sample followed by the screen. Slide the top of the permeameter onto the threaded rods and down onto the sample. Check to see that the O-rings are properly seated befroe tightening down the wing nuts.

6. Tighten down all wing nuts using a wrench or pair of pliers. Do not damage the threads on the rod.

Beginning the Test:

7.
   - o Attach the permeameter chamber to the high pressure hose with the quick connect attachment.
   - o Both brass valves on the chamber should be open.
   - o Overflow valve (plastic handle) on chamber should be closed.
   - o Valve 25 B is closed (the valve on the compressor side of the regulator).
   - o The pressure on the gage at 0 psi.
   - o Valve 23C opened (allows water to flow into measuring burette attached to reservoir).

   Using a crescent wrench, open the filling nut on the top of the reservoir; add distilled water to the chamber until the level in the burette reads at least 8. Replace and tighten the filling nut.

   - o Valve 23C closed.

   Now begin to apply the pressure to the sample:

8.
   - o Valve 25 B opened.

   Increase the pressure at the permeameter SLOWLY to avoid breaking the o-ring seals. Increase the pressure in roughly 10 psi increments every 30 minutes to an hour.

   - o Turn regulator CLOCKWISE to INCREASE pressure to first increment. Note the date, time and pressure arrived at on the data sheet.

Continue to apply increments of pressure until the desired head has been reached. Never exceed 60 psi.

9. Before and after each pressure change, check the chambers for leaks. If one is found, do not increase the pressure until it has been eliminated. It may be necessary to decrease the pressure, wait a while and then increase it again. Make sure that all the wing nuts are tight. It may be necessary to remove the pressure and re-assemble the chamber.

   Only very small leaks (1 drop every few minutes) on the high pressure side of the sample may be ignored. Leaks of any magnitude on the low pressure, or burette, side of the sample will significantly affect the burette readings.

<u>Obtaining The Data</u>:

Once the desired pressure has been reached in the chamber, it may take several days for the water to saturate the sample and flow into the burette. The magnitude of that flow is what will now be measured.

10. Once water rises above the "0"-mark in the burette, note the date, time, and reading on the data sheets. Because burettes are scaled in both directions,it is important that the bottom always be considered "0" and the top "10". This makes calculations easier.

11. Take burette readings at regular intervals. Use a timer if necessary to remind yourself to take the reading. The length of time between readings depends on the quantity of the flow: a minimum of 5 units on the burette (5 ml) between readings is desired.

12. When the water level in the burette nears full, lower it by means of a piece of plastic tubing that can be slid inside of the burette.

LABORATORY TESTING PROCEDURES

Ending the Test:

13. When consistent values of K have been obtained for at least 3 readings, the test may be stopped.

    - Valve 25B closed
    - All valves on the chamber closed
    - Reduce pressure to 0 psi
    - Open plastic pressure relief valve on permeameter chamber and allow water to escape into a container
    - Disconnect quick-connect attachments, remove chamber carefully to the side. BE CAREFUL OF THE BURETTE.

14. Weigh the mold with the soil in it, and record under "weight compacted - after" on the data sheet.

15. Now use the sample ejector to remove the sample from the mold. Place the sample in a large drying pan. Slice the sample longitudinally in half and remove two moisture content samples from the middle. It is normal for soil near the high pressure end of the sample to appear much "muddier" than the rest - this is due to the sample re-expanding when the pressure was removed. This is not representative of the test conditions; do not take the moisture content samples from here.

16. Conduct the moisture content determination as usual, entering the data in "moisture content - After" on the data sheet.

17. Finish disassembling the apparatus. Clean and set aside to dry.

RECOMPACTED PERMEABILITY

Project No.: ____________ Date Started: ____________
Project Name: ____________ Tested by: ____________
Sample Number: ____________ Lab I.D.#: ____________
Location of Sample: ____________

Type of Test: ____ Standard ____ Modified
Method: ____A ____B ____C ____D

Optimum Moisture Content: ____________ Maximum Dry Density: ____________

MOISTURE CONTENT:

	Before			After	
Container #			Container #		
W_{wc}			W_{wc}		
W_{dc}			W_{dc}		
W_c			W_c		
w%			w%		
% Optimum			% Optimum		

DRY DENSITY:

Mold # ____________ Weight of Mold ____________

	Before		After
Weight Compacted		Weight Compacted	
Dry Density		Dry Density	
% Maximum		% Maximum	

Length of Sample in 6" Mold: ____________

Parameters:	6"		4"		Harvard Miniature	
Volume, ft^3 (cm^3)	.075	(2124)	.033	(944)	.0022	(62.3)
Cross-sectional area, in^2 (cm^2)	28.3	(182.4)	12.6	(81.1)	1.33	(8.55)
Nominal Length in (cm)	4.58	(11.6)	4.58	(11.6)	2.8	(7.11)

1 psi = 70.3 cm. Water

D. CALCULATIONS

The two variables T and V merely indicate the change in time (time elapsed) and volume (amount of water in the burette) since a previous reading. T should be expressed in seconds, and V in ml.

The flow rate $Q = V/T$

The coefficient of permeability K is defined as follows:

$$K = \frac{QL}{AH}$$

Q = Volumetric flowrate, ml/Sec (= cm^3/sec)
L = Length of the sample in the chamber, cm.
A = Cross-sectional area of the sample in the chamber, cm^2
H = Head of water across the sample, cm;

$$H = 70.3 \times P$$

P = Pressure in the chamber in PSI

LABORATORY TESTING PROCEDURES

Sheet 2 of 2

RECOMPACTED PERMEABILITY

READINGS

Site: ____________________ Project No. ____________________

Tested by: ____________________ Project Name ____________________

DATE	PRESSURE	TIME	ΔT	READING	ΔV	Q	K

APPENDIX C-2

TEST METHOD FOR UNDISTURBED SHELBY-TUBE HYDRAULIC CONDUCTIVITY (PERMEABILITY) TEST

LABORATORY TESTING PROCEDURES

UNDISTURBED PERMEABILITY TEST USING THE FLEXIWALL PERMEAMETER

A. EQUIPMENT

Permeameter Chamber
Permeameter Burette Panel
Permeameter Master Panel
Flexible Membrane
Membrane Tester
Membrane Stretcher
Balance
Knife
Silicon Grease
Distilled Water Supply

B. PREPARATION

The equipment used in this test is very valuable - IT MUST NOT BE MISUSED.

This test requires a skilled operator - if at any time you are uncertain of how to proceed, ask someone.

This test may be combined with a determination of porosity. If this desired, notes in the test explain what steps must be taken.

C. PREPARE SAMPLE

1. Remove sample from shelby tube using the extruder being careful not to let sample crack or break.

2. Cut a representative 6" or less length of the sample, place on a cutting board, and trim to approximately 2.8" in diameter, the dimension of the porous discs in the permeameter. An easy way to gauge this width is to place a piece of that sized filter paper on the top and the bottom of the sample. After trimming, the sides should be straight, and the top and the bottom MUST be flat and parallel to the surface of the countertop.

LABORATORY TESTING PROCEDURES

De-Air the Porous Discs

3. If the porous discs are dirty, clean them by placing them in boiling distilled water for at least 15 minutes.

4. To de-air the discs, first remove the top of the permeameter chamber and set it carefully aside. Move the upper platen out of the way, being sure not to crimp it's hoses. Next, apply a thin coat of silicon vacuum grease to the upper sides of the lower platen. Assemble the vacuum saturation device (tube, rubber stopper, plexiglass tube) and attach it to the vacuum hook up on the master control panel. Insert a porous disc into the plexiglass tube and slide this onto the lower platen.

5. Now flood the disc with about 1/2" of water by filling the lower burette (the burette for the lower platen) on the burette panel with water and emptying it onto the lower platen:

   o all valves on chamber closed
   o all valves on burette panel to "off" or "vent"
   o V3 to "fill"
   o L2 to "fill/drain" till burette is full, then off
   o CL1 opened till burette is nearly empty, then closed.

   If necessary, repeat this procedure till 1/4"-1/2" of water is standing above the porous disc inside the plexiglass tube.

6. Now apply a gentle suction to the device till bubbles rise from the disc and around it's edge. Be careful that the rubber stopper is not sucked down into the plexiglas tube. When no more air comes from the disc, but only from around the edge, stop the suction. Remove the device from around the platen, letting the water be caught on the chamber base. Set the porous disc in distilled water and repeat the procedure for the second disc.

LABORATORY TESTING PROCEDURES

Prepare Membrane

7. First, check membrane for leaks. Slide the membrane over the membrane tester and secure the ends with O-rings or rubber bands. Immerse totally in water and blow gently through the tube. Any leaks in the membrane should be easily seen.

Mount Sample

8. Assemble the membrane stretcher. Put two O-rings (and/or rubber bands) around the membrane stretcher, one above and one below the tube inlet. Remove the membrane from the tester and place it inside the stretcher. cover the inside hole in the stretcher with a piece of wet filter paper or paper towel to help evenly distribute the suction. Roll the ends of the membrane back around the outside of the stretcher. Now apply a gentle suction to the tube and check that there are as few twists and wrinkles in the membrane as possible. Apply enough suction to pull the membrane flat against the inside of the stretcher.

9. Place a piece of wet filter paper on the top and bottom of the trimmed sample. Remove a porous disc from the water and place it on the lower platen. Squirt this down with distilled water and place the sample, with filter paper, on top of the disc. Now slide the membrane stretcher, with the membrane pulled against the insides, over the sample and onto the chamber base. Place the second porous disc inside the stretcher, on the filter paper on top of the sample. Release the suction on the membrane and roll the membrane ends off of the top and bottom of the stretcher. Roll the O-rings off the stretcher onto the membrane, but not around the sample. Remove the membrane stretcher from around the sample.

10. Now gently place the upper platen on top of the porous disc and roll the membrane up around the platen. Ensure that there are as few

wrinkles and twists in the membrane as possible. Position the O-rings around the membrane roughly midway along the platens and CAREFULLY trim off the excess rubber that extends beyond the platens. Do not trim below level of platens.

Assembling and Filling the Chamber

11. Check that the large O-ring around the chamber base has a thin coating of vacuum grease. Open the pressure release valve on the chamber top. Slowly position the top onto the bottom, taking care not to catch the hoses or knock the sample. The two halves should join snuggly.

12. Attach the clamp around the joint between the two halves. Make sure that this fits properly.

13. The chamber can now be filled with water:
    - all pressures on the master panel are 0 psi
    - all valves on the burette panel are "off" or "vent"
    - all valves on the chamber are closed
    - V3 to "fill"
    - C2 to "fill/drain"
    - Open top pressure release valve
    - Open CCI till the water flows out of the top pressure release valve, then close both CCI and pressure release valve.
    - C2 to "off"

    The chamber will fill under gravity feed from the distilled water source, and will do so slowly, in approximately 10-20 minutes.

Apply Seating Pressure

The next several steps are designed to remove air trapped in both the system and the sample.

14. To apply seating pressure, first the three burettes must be filled:
    - o all pressures on the master panel at 0_{psi}
    - o all valves on the chamber closed
    - o all valves on the burette panel to "off" or "vent"
    - o V3 to "fill"
    - o C2, V2, L2 to "fill/drain: till burettes are nearly full, then "off".

15. Next apply seating pressure of 2-3 psi to the chamber and permit air to drain:
    - o V1 on master panel to "Chamber"
    - o use regulator RC to set 2-3 psi for the chamber as seen on gauge GM
    - o C1, C3 to "on"
    - o CC1 opened
    - o C~~V~~u2, CL2 opened till no more air flows out, then closed
    - o CC1 closed
    - o C1 to "~~off"~~ vent
    - o C3 to "~~vent"~~ off

Flushing porous discs

To flush the porous discs, water must be supplied to them through the burettes. (This is also the way that water will be sent to the sample during the test. No water can reach the patens, the porous discs, or the sample, unless there is a leak except in the two stage process described here.)

16. First, the burettes must be filled.
    - o all valves on the chamber closed
    - o all valves on the burette panel to "off " or "vent"
    - o V3 to "fill"
    - o V2, L2 to "fill/drain" till burettes are nearly full, then "off".

17. Then, the water must be allowed into each porous disc, and other through that disc's drainage line. Thus any air in the discs or fill lines should be forced out. Be sure that at no time do the burettes empty of water, as this may allow air into the lines. This requires caution as the burettes will drain in several seconds.
    - CL2 opened
    - CL1 opened till the burette is nearly empty, then closed
    - refill the burette as described above and repeat the procedure several times.

In between the steps, check the supply lines to the upper and lower platens, inside the chamber and outside, for air bubbles, Gently tap on the lines to encourage the bubbles to move through the system. These must be removed before the test can proceed. When the air has been removed:

- CL1 closed
- CL2 closed
- repeat the above procedure for the upper burette and platen.

NOTE: At this point, the sample is ready to be back-pressured and consolidated, with either occurring first. Back pressuring first has the advantage of providing more accurate volume change measurements during subsequent consolidation. This procedure is necessary if precise porosity measurements are desired. Consolidating first has the advantage that fluid flow out of the specimen will carry remaining air with it. The latter procedure will be described here. This is the desired method unless otherwise noted. Only minor modifications in procedure are necessary if the reverse order is called for.

Consolidation

18.
    - all valves on the chamber are closed
    - drain burettes till roughly half full
    - all valves on burrette panel to "off" or "vent"
    - V1 to "chamber"
    - set desired consolidation pressure _____
      (This should be roughly 10 psi)
    - Open C1 and C3
    - Open CC1

19. If consolidation records are desired, note the levels in the burettes.

20. simultaneously open CU1 and CL1

The chamber pressure is now forcing excess water out of the soil sample. Because the samples is relatively incompressible, the change in the water levels of the lower and upper burettes should be slow. A rapid rise in either indicates a leak between the chamber and that platten. The necessitates disassembling the chamber and tightening the connections or replacing the membrane

21. Watch the water levels in the burettes, that they do not empty or overflow. If they should near this state, close all valves on the chamber, and turn all valves on the burette panel to "off" or "vent", before refilling or draining the burettes.

22. When consolidation is completed, no further change will occur in any burette level. At this time:

- close all valves on the chamber
- all valves on the burette panel to "off" or "vent"

Back Pressuring

This is the final preparatory step before conducting the acutal test.

23. A back pressure is an equal pressure increment applied to both the chamber and specimen drainage lines; in order to avoid damaging the specimen, the back pressure should be applied in relatively small increments, with sufficient time for pore pressure equalization between applications; increments of 10 psi at 30 minute intervals are recommended. The back pressure will create a flow of water through the specimen which will carry all remaining air with it.

- All valves on the chamber closed
- Fill chamber and lower burettes until nearly full. Drain upper burette till nearly empty.
- All valves on burette panel to "off" or "vent".
- Apply low pressure (3-5 psi) to upper using V1, RU and GM.
- U~~V~~1 to "on"
- Apply slightly higher pressure (7-10 psi) to lower
- L1 to "on"
- Apply a pressure higher than the others (13-15 psi) to the chamber
- C1 and C3 to "on"
- Record burette levels
- CC1 opened
- CL1 and CU1 opened simultaneously

24. Periodically record burette levels and then increase pressure in all three burettes by the given increment (approximately 10 psi). The water level in the burettes must never be allowed to empty.

25. If any burette nears empty:

    - All valves on chamber closed
    - Flow valve on burette panel corresponding to the empty burette to "vent"
    - Fill burette
    - Flow valve to "on"
    - Open CC1
    - Open CV1 and CL1.

26. Gage GM must be used to monitor pressures because the smaller gages are not sufficiently precise. After 2-4 increments have been applied, maintain final pressure level for several hours, or until burette levels have stabilized. Then conduct the final check for air in the system:

- CU1 and CL1 closed
- V1 and L1 to "vent"
- Fill upper and lower burette to equal levels near the top of the burettes
- V2 and L2 to "off"
- Record burette levels
- CV1 and CL1 opened

27. If burette levels deflect significantly, air is present in the system. Repeat the back pressuring procedure.

28. If burette levels do not deflect, the specimen is ready to be tested.

    - All valves on the chamber closed
    - All valves on the burette panel to "off" or "vent"
    - All pressures on Master Panel to "0".

Testing

The pressures should be applied to the specimen in the same order and the same relative magnitude that they were in the back pressuring procedure.

29. Commonly used guidelines for determining the magnitudes of the pressure are:

    - The pressure differential should not exceed 50 to 75% of the consolidation pressure [(P lower - P upper) § (.50 to .75)(P chamber - P upper)];
    - The pressure in either specimen drainage line must not exceed 90% of the chamber pressure;
    - The pressure in either specimen drainage line must be at least 5 psi less than the chamber pressure.

30. Set the pressures using V1, GM and the appropriate regulator. When they have been set:

    - Ensure that the chamber burette is near mid-level, lower burette is nearly full and the upper burette is nearly empty.
    - C1, C3, V1 and L1 to open
    - CC1 opened
    - CV1 and CL1 opened simultaneously
    - Record burette levels, the date and time.

31. Never allow burettes to empty - when they are close to emptying (or overflowing) follow the procedure in "Back Pressuring" for refilling or emptying them.

Periodically record the burette levels, date and time.

32. When consistent flow valves have been attained, the test may be stopped. This may take a full day or longer.

33. If the test must be left overnight:

    - All valves on the chamber closed.
    - All valves on the burette panel to "off" or "vent".
    - All pressures to "0" psi.

34. The following morning, return the pressures to their proper level, open C1, C3, U1 and L1; then open CC1 followed by CU1 and CL1.

Ending the Test

35. Once consistent flow valves have been attained for a reasonable period, the test may be stopped.

    - All valves on the chamber closed
    - All valves on the burette panel to "off" or "vent"

- o All pressures to "0" psi
- o Open pressure release valve on the top of chamber
- o Disconnect chamber from the burette panel at QC, QV and QL. Be careful of the teflon tubes - they kink easily, and this impairs their performance.

36. Drain the water from the chamber:

    - o Remove the tube at CC1 and open the valve into a container;
      or
    - o Place the chamber in a large drying pan and carefully remove the clamp and the top of the chamber.

37. Remove the specimen carefully and take two moisture content readings if needed. (If needed for porosity calculations, measure the volume of the specimen and its weight before taking the moisture sample.)

38. Carefully clean the chamber as needed and set aside to dry. Discard the membrane used; be careful not to lose the O-rings. Clean the porous discs by boiling for 5-10 minutes.

Calculations

40. The purpose of any permeability test is to compute the coefficient of permeability of the soil being tested.

    With large pressure gradients across the sample, say greater than 20 psi, the calculations are quite simple. However, the gradient employed here is usually less, roughly 7 psi. At this low level, the pressures exerted on the sample by the columns of water in the burettes become significant. Thus the coefficient of permeability must be calculated using the falling head equation:

$$K = \frac{a \cdot L}{A(t_2 - t_1)} \ln \frac{h_1}{h_2}$$

LABORATORY TESTING PROCEDURES

K = coefficient of permeability cm/sec
a = cross-sectional area of the burette
A = cross-sectional area of the sample
h_1, h_2 = total system head at times t_1 and t_2 across the sample

a = .941 cm^2 for the 25 ml burette
= .121 cm^2 for the 3 ml burette

SECTION 1. SYSTEM DESCRIPTION

The new Deluxe Flexi-Wall Permeameter system is designed to accurately determine permeabilities of clay soils. The system includes essentially three basic components: master control panel, burette panel and chamber. In addition the Toxic Flexi-Wall Permeameter includes two pressure interface chambers for use with the burette panel.

1.1 Master Control Panel

This is the 'heart' of the system and is required to control and monitor permeability tests. This panel features three controllable pressures (up to 100 psi) and comes fitted with ports for directly supplying to the burette panel. Three small gauges show the values of each air pressure output at all times while the master gauge, accurate to 1/4 psi, is used for accurately setting and measuring the applied pressures. An air-driven vacuum pump built into the master panel provides facility for vacuum saturation of the specimen. There are two differential pressure regulators, one standard pressure regulator and one -30 to +30 psi differential pressure gauge on the panel. The differential pressure between chamber and lower burette or that between lower and upper burette can be selectively set and read on the differential gauge by operating appropriate valves. The vacuum generated by the vacuum transducer can also be read on the same gauge. The precision morter gauge provided on the panel can be used to precisely set and read any of the pressures.

1.2 Burette Panel

The burette panel contains three 25 ml burettes and a 3 ml burette. One 25 ml burette is connected in parallel with the 3 ml burette for outflow measurement.

Functionally, the burette panel consists of two air/fluid circuits, namely a chamber circuit (sometimes called the "cell", "confining", or "lateral" circuit) and a sample fluid circuit.

The sample fluid circuit contains two 25 ml burettes and one 3 ml burette which act as air/fluid interfaces in addition to permitting measurement of flows into and out of the sample (or specimen). In normal operation, the "upper" and "lower" burettes are connected to the top and bottom of the sample, respectively. The Forward-Reverse valve (V2) permits reversing the direction of flow during a permeability test. The air lines leading to the burettes are fitted with traps for isolating permeant and protecting upstream components in the event of overflow. The fluid collecting in the traps will be drained automatically through the float valves at the bottom which open when the pressure of air in the traps changes in the operation of the system anytime. The valves upstream of the burettes (U1, L1) are used to both apply and vent the burette pressures. The two-position valve (V3), external fill line and downstream valves (U2, L2) are used for adjusting the fluid levels in the burettes or introducing permeant during a test.

One 25 ml burette serves as the chamber reservoir. The chamber reservoir is the air/fluid interface for pressurizing the sample confining chamber. Finally, three ports fitted with quick-connects (QC, QU, QL) are provided for convenient connection of the permeameter chamber to the burette panel.

1.3 Permeameter Chamber

The chamber accomodates 2.8 in. diameter (nominal) specimens up to 6 in. in length and features "zero displacement" valves on the specimen drainage lines and a flushing circuit for saturating the porous discs. Platens for 2.5 in. and 4 in. diameter specimens are available as options.

A schematic of the permeameter chamber is presented in Figure 3. A valve (CC1) and bleed valve (CC2) provide access to the chamber. The upper and lower sample drainage lines are fitted with pairs of valves (CU1, CU2, CL1, CL2) enabling convenient flushing of the porous discs. The figure shows quick-connect tubes attached to valves CU1, CL1, and CC1.

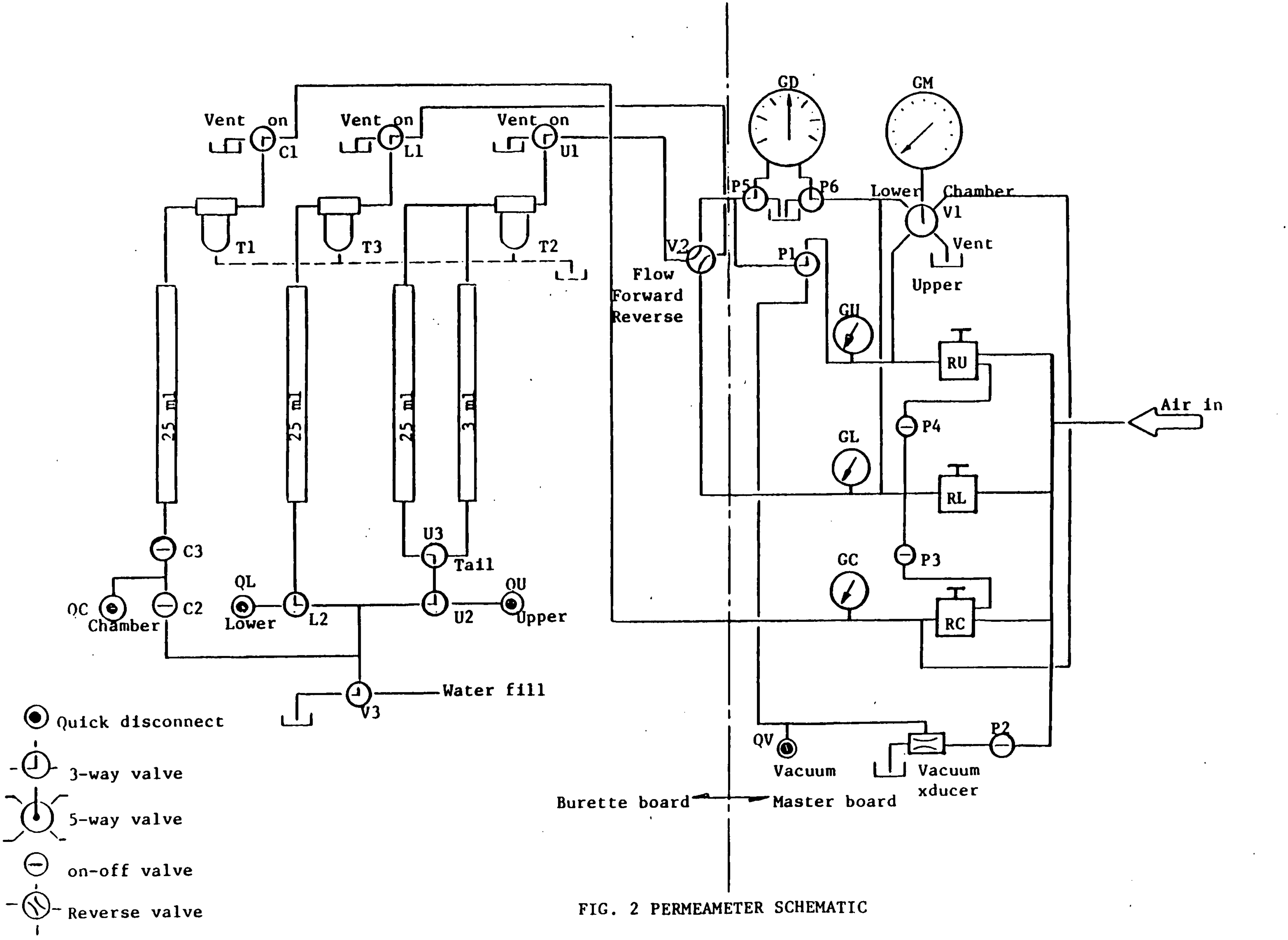
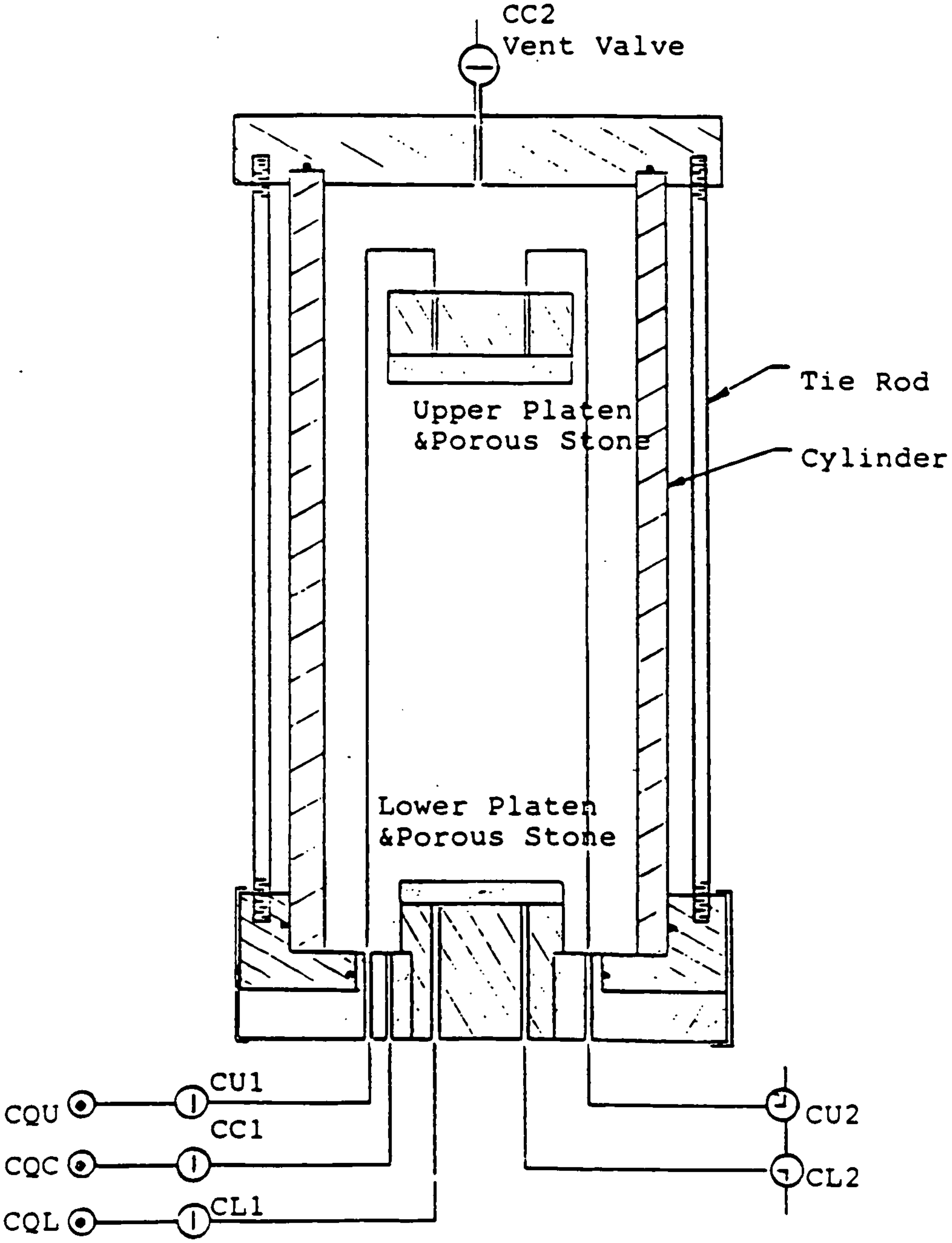


FIG. 2 PERMEAMETER SCHEMATIC



SCHEMATIC OF PERMEAMETER CHAMBER
FIG. 3

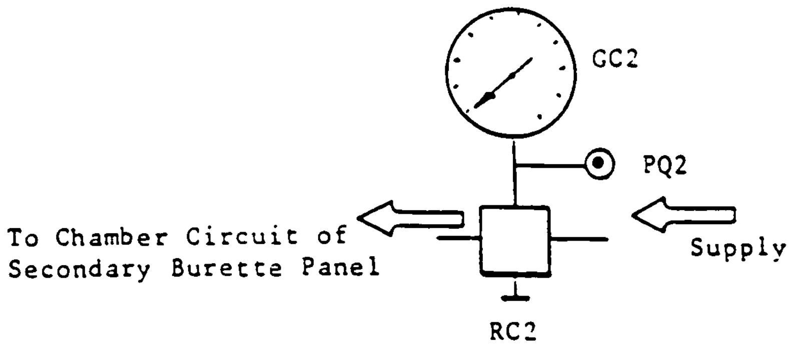


FIG. 4. AUXILIARY CONTROL PANEL

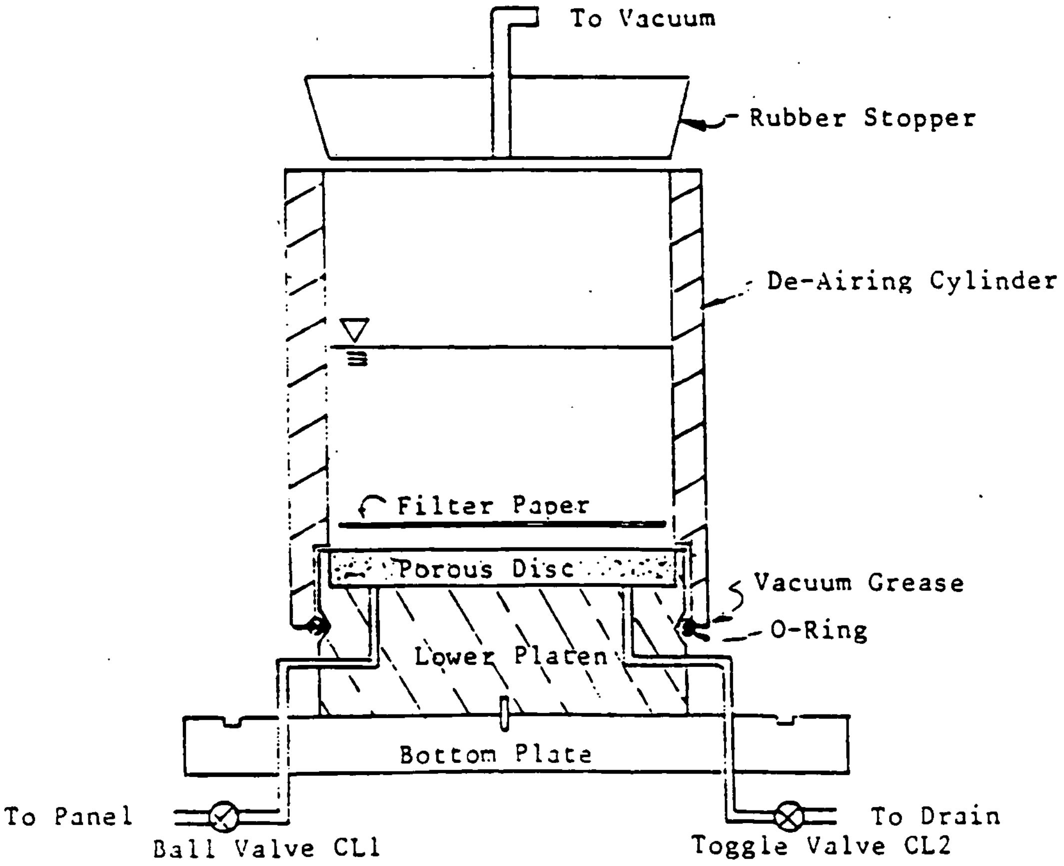


FIG. 5. DE-AIRING BOTTOM POROUS DISC, FILTER PAPER AND LINES (PROCEDURE SIMILAR FOR TOP)

APPENDIX D

METHOD FOR DETERMINING ACCEPTABILITY OF COMPACTION VIA IN-SITU NUCLEAR DENSITOMETER TESTING

METHOD FOR DETERMINING ACCEPTABILITY OF COMPACTION VIA IN-SITU NUCLEAR DENSITOMETER TESTING

The barrier layer soil compaction process will be monitored as the quality assurance mechanism for achieving desired barrier layer soil permeability. The compaction process will be monitored through routine determination of the soil moisture content and density of the lift being constructed using a nuclear densitometer. Maintaining the soil moisture content and density combination within an "acceptable zone" will facilitate achieving desired barrier layer soil permeabilities.

During barrier layer construction, the measured in-situ dry density immediately following barrier layer soil compaction shall be at or greater than ninety percent (90%) of the maximum modified Proctor dry density determined for the barrier layer soil. Noted exceptions include locations where compaction efforts necessary to achieve this density would damage underlying flexible membrane liners, geonets or geotextiles or otherwise compromise their intended function.

Measured in-situ moisture content and density will be considered acceptable as long as eighty percent (80%) of the data plot above a line which is determined by the line of optimums less two (2) percent moisture on a graph of the most recent representative modified and standard Proctor curves and all of the data plot above a line which is determined by the line of optimums less four (4) percent moisture on this same graph. The line of optimums shall be a curve which passes through the maximums of both the standard and modified Proctor curves and is parallel to the curve of zero air voids. A typical moisture-density graph (Proctor curve) is attached as Figure D-1.

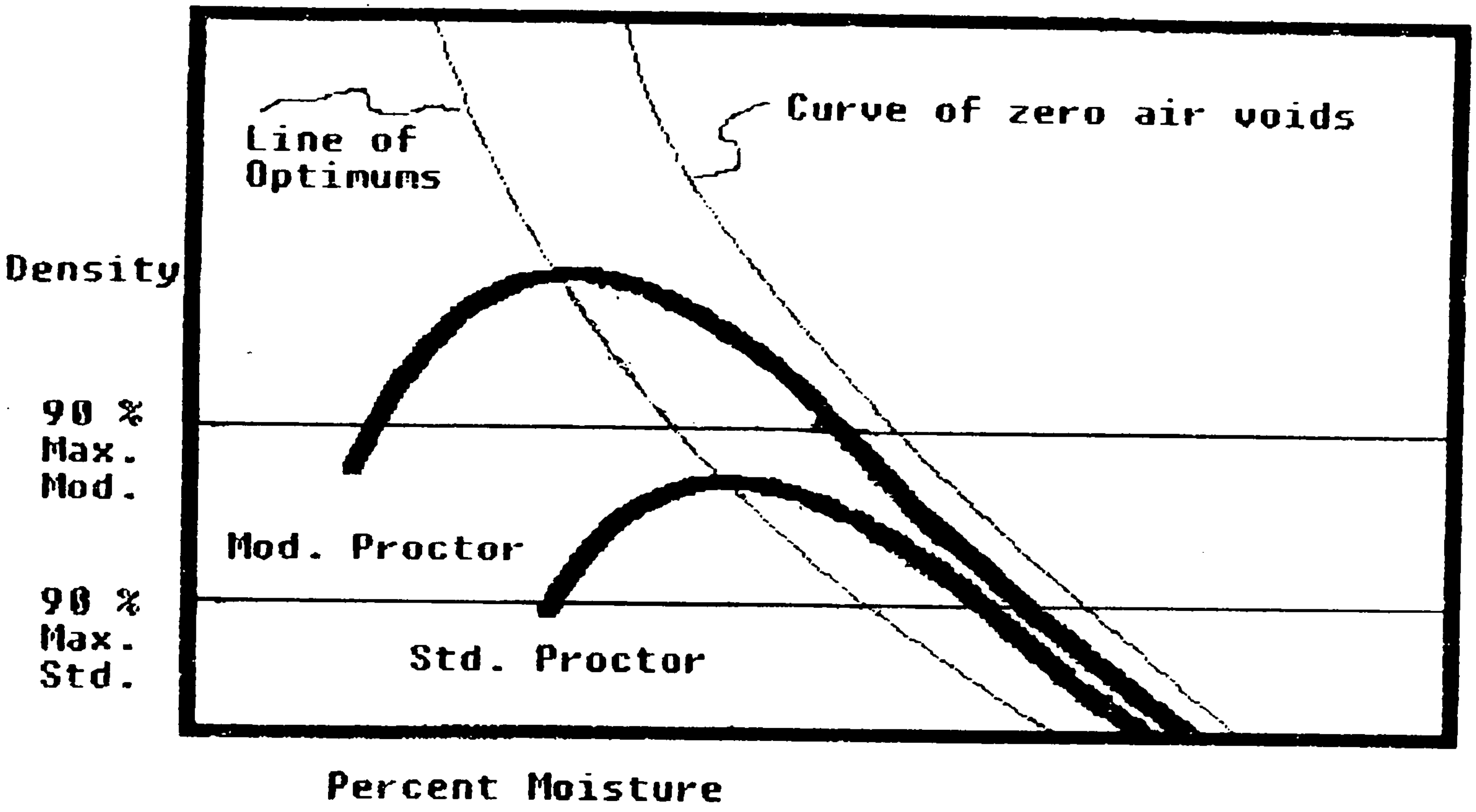

Line of Optimums
Curve of zero air voids
Density
90 % Max. Mod.
Mod. Proctor
90 % Max. Std.
Std. Proctor
Percent Moisture

FIGURE D-1

APPENDIX E

RESUMES OF QA PERSONNEL

MALCOLM PIRNIE

PAUL H. WERTHMAN
Vice President

EDUCATION

BS (Environmental Engineering) 1975; Rensselaer Polytechnic Institute
ME (Environmental Engineering) 1977; Rensselaer Polytechnic Institute

REGISTRATION

Professional Engineer

SOCIETIES

New York Water Pollution Control Assoc.
Water Pollution Control Federation
American Institute of Chemical Engineers
American Consulting Engineers Council
Solid Waste Management Association
New York State Business Association

RECOGNITION

Author: Articles and presentations on industrial wastewater treatment, solid and hazardous waste management.

AWARDS

1989 - Young Principal of the Year - New York Chapter American Consulting Engineers Council

SUMMARY OF EXPERIENCE

Mr. Werthman has over 12 years of responsible experience in hazardous and solid waste management; leachate and wastewater treatment process evaluation; landfill siting, permitting, design and construction management; hydrogeologic and soils investigations; and environmental assessment. He has served as Malcolm Pirnie's chief regulatory negotiator having successfully secured fourteen (14) solid waste facilities permits and/or Orders on Consent from New York State Department of Environmental Conservation. He has served as technical expert in presenting testimony regarding solid and hazardous waste management facilities and regulations before public meetings, public hearings, and government bodies and siting boards. Mr. Werthman is primarily responsible for the establishment and continued operation of the firm's Soils Laboratory. His primary roles as Project Officer on solid waste projects are technical quality assurance, contract management, and supervision of over twenty-seven (27) technical staff involved in solid waste projects.

DETAILED EXPERIENCE

1979 to Date — Malcolm Pirnie, Inc.

As Vice President:

- Certified complete the closure of the Five-Points Landfill for the County of Cattaraugus. The $1.12 million project was completed on time, below the bid price.

(over)

DETAILED EXPERIENCE (Continued)

1979 to Date Malcolm Pirnie, Inc. (continued)

- Certified complete the construction of the soil and synthetic double liner system and leachate storage/loading facilities for the first (6.5-acre) cell of the Bath Sanitary Landfill No. 1 for the Steuben County. The Permit to Operate was issued just 3 months after ground was broken.

- Performed value engineering evaluation of retrofit leachate collection system design prepared by another engineering firm for the Lindley Sanitary Landfill and Bath Sanitary Landfill No. 1 (listed NYS inactive hazardous waste sites) for Steuben County. Based upon the value engineering evaluation, major redesign was performed.

- Currently managing a study for a consortium of twelve New York State paper industries to justify their solid wastes as a special classification of industrial waste under NYCRR Part 360-2.14 with an attendant reduction from landfill liner (i.e. double composite) design requirements.

- Provided technical oversight of project-related research in the Soils Laboratory addressing: freeze-thaw impacts on clay soils; leachate compatibility, and; chemical constituent leaching from contaminated soils.

- Supervised a field-intensive evaluation of capping/contaminant alternative for closure of a 20 acre inactive RCRA landfill for an industrial client. The field investigations utilized soil borings, piezometers, wells, and lysimeters to collect physical, chemical, and hydrogeologic data used in an extensive mathematical model to predict pollutant loadings to groundwater and surface water from the site under various closure scenarios. The closure plan, currently under design, is estimated to save approximately $4 million relative to the conventional RCRA cap.

As Senior Project Manager:

- Negotiated an Order on Consent which allowed two years of additional operation while lateral expansion was evaluated for the Formso Landfill in the Town of Perry, NY; Supervised the planning, design, permitting and construction administration of the sanitary landfill vertical expansion and closure. Closure plans were approved in accordance with 6NYCRR, Part 360 regulation and included: modifications to the groundwater monitoring system; leachate collection system retrofit, and; surface water control.

- Supervised the preparation of a Part 360 Closure/Post-Closure/Operation Plan for Cattaraugus County's Five Points Landfill, a construction and demolition debris site, in the Town of Mansfield, NY. The approved phased plan allowed the use of soils mined and screened on site, saving the County approximately $100,000 - $200,000.

(over)

DETAILED EXPERIENCE (Continued)

1979 to Date Malcolm Pirnie, Inc. (continued)

As Project Manager:

- Supervised the planning, design, permitting and construction administration of wide-trench sanitary landfill for disposal of vacuum-filtered and pressure-filtered tannery wastewater treatment plant sludge in conformance with Title 6, NYCRR Part 360.
- Supervised the preparation of design plans and specifications, engineering report, an environmental assessment and hydrogeological investigation for two of Niagara Mohawk Power Corporation's proposed landfill sites for fly ash disposal.
- Responsible for the hydrogeologic investigation of a 48-acre section of the Great Baehre Conservation Area that was used as a municipal landfill. Remedial measures were evaluated so it can be used as a recreational area.
- Responsible for hydrogeologic investigations of 4 inactive industrial landfills for confidential NY clients.

As Senior Project Engineer:

- Siting, permitting and preliminary design of proposed 365-acre landfill for Amherst, NY wastewater treatment plant sludge and incinerator ash. Unique design features included low-profile cells, high groundwater conditions, synthetic liner with leachate collection system, and small diameter, low-pressure sewer for conveyance of leachate to the Town wastewater treatment plant.
- Evaluated feasibility of alternative sludge handling and disposal methods; site selection; environmental impact analysis; preliminary design and permitting of special purpose sludge landfill for Niagara Falls, NY combined industrial/municipal wastewater treatment plant. The landfill was designed completely above-grade with an integrated leachate/surface water collection system with clay and synthetic bottom liner.
- Hydrogeologic investigation and/or groundwater monitoring system design and evaluation at 6 sites in Western New York.
- Preparation of closure plans for two hazardous waste landfills and two sanitary landfills in New York State.

1979 Frontier Technical Associates

As Project Engineer:

- Hydrogeologic assessment of abandoned industrial solid waste disposal site for confidential NY client.

(over)

DETAILED EXPERIENCE (Continued)

1976-1979 Calspan Corporation

As Project Engineer/Engineer

- Supervised soil testing laboratory. Performed study of attenuation on soil of heavy metals from industrial wastewater sludge. Designed groundwater monitoring systems; and conducted hydrogeologic investigations and soil analyses at abandoned industrial and hazardous solid waste disposal sites.

PRESENTATIONS/PUBLICATIONS

"An Investigation of Uranium Mill Wastewater Treatability," Proceedings, Purdue Industrial Waste Conference, May 1980.

"Granular Activated Carbon Removal of Priority Pollutants in a Combined Municipal/Industrial Wastewater," Proceedings, 39th Annual Purdue Industrial Waste Conference, May 8, 1984.

"Liability Control Through Waste Minimization: The Audit As a Waste Minimization Tool," Proceedings, Sixth Annual Greater Buffalo Environmental Conference, September 1988.

"Monitoring Ground Water Systems", Proceedings, AWWA-NY Section, September 22, 1982.

"Treatment of High-Strength Organic Chemical Industry Wastewaters in a Sequencing Batch Reactor," Proceeding, Water Pollution Control Federation, October 1988.

"VOC's In Ground Water," Proceedings, AWWA-Western NY Section, October 6, 1982.

Werthman, P.H., et al, "Industrial Waste Contamination of a Water Treatment Plant Site: A Case Study"

Werthman, P.H., et al, "Residual Management at a Combined Industrial/Municipal Wastewater Treatment Plant"

WESLEY C. DUST
Associate

EDUCATION

AS Engineering Science 1973; Erie Community College; Buffalo, New York
BS Civil Engineering 1975; State University of New York at Buffalo

REGISTRATION

Professional Engineer

SUMMARY OF EXPERIENCE

Mr. Dust has more than 13 years of responsible experience in structural design, coordinating of structural systems, construction inspection/ administration and system testing.

DETAILED EXPERIENCE

1985 to Present   Malcolm Pirnie, Inc.

As Associate: Responsible for coordination of construction administration, resident inspection and field survey work for the Buffalo Regional Office. In charge of staffing, oversight, and contract procurement for landfill, water and wastewater construction projects.

- Directed installation of the leachate collection system and closure of the 25-acre Town of Batavia, NY, Sanitary Landfill, including closure contract procurement.

- Responsible for coordinating manpower, construction administration and resident inspection for the 25-acre Formso sanitary landfill expansion and closure in Perry, NY.

- Supervised certification, construction administration, inspection and testing for closure of the 16-acre Farwell sanitary landfill and installation of the leachate collection system for the Cattaraugus County Department of Public Works.

- Directed the construction administration and resident inspection phases of the closure of 16-acre active portion of Cattaraugus County's Five Points sanitary landfill in Mansfield, NY.

- Directed the redesign effort and construction administration of 14-foot diameter deep rock tunnels for combined sewer storage and transmission for the Rochester Pure Water Tunnels. (Project cost $39.5 million)

- Project Manager on all Erie County Water Authority projects. List includes Wehrle Tank, Hamburg Eden pipeline, computerization of distribution system and various smaller pipelines.

(over)

DETAILED EXPERIENCE (Continued)

- Responsible for the design modifications and construction administration of a 0.5 average daily flow water treatment plant. This work includes modifications to the Village of Gowanda reservoir.
- Responsible for coordinating the construction administration and resident inspection phases of the Lancaster/Alden pipeline project for the Erie County Water Authority. This includes 46,300 feet of 20" pipeline and an elevated storage tank.
- Responsible for construction administration and resident inspection for three simultaneous Erie County Water Authority projects: Sandridge/ Wende is 20,100 LF of 20" pipeline; Broadway/Sandridge is 14,450 LF of 16" pipeline; and the construction of 3500 LF of 12" and 3800 LF of 20" pipeline for the Walden/ Wende Contract.
- Supervise the construction administration on 2.5 miles of waterline in the Town of Hamburg, New York.
- Supervise the bid procedures and construction of the Boston Valley, NY pump station for the Erie County Southtowns Sewage Treatment Agency.

1983 - 1985 Birdair Structures

As Project Engineer:

- Responsible for the design, fabrication and erection of a $5.5 million tensioned-fabric roof structure for Canada Place - Expo '86, Vancouver, Canada.
- Produced the design and supervised the fabrication and erection of a $1.2 million tensioned-fabric roof for a bus terminal in Shreveport, Louisiana.
- Responsible for the design, fabrication and erection of a $800,000 tensioned-fabric roof structure for a mall in Tulsa, OK.

1981 - 1983 Malcolm Pirnie, Inc.

As Engineer: Responsible for all structural design and related coordinator of structural systems.

1975 - 1980 Black & Veatch Consulting Engineers
Kansas City, Missouri

As Engineer: Responsible for all phases of structural engineering including layout analysis and design of various structural systems. He was involved in fossil-fueled and nuclear power plant projects which included turbine buildings and pedestals, intake structures, and coal transfer stations. Projects have included a desalinization plant, industrial facilities and water and wastewater plants.

(continued)

DETAILED EXPERIENCE (Continued)

1975 - 1980	Black & Veatch Consulting Engineers Kansas City, Missouri (continued)

Mr. Dust was also the resident engineer for the 20 MGD secondary sewage treatment plant in Billings, Montana. The secondary facilities consisted of a settled sewage pumping station, four aeration and final settling basins, two chlorine contact basins and two flotation thickening basins. The project also consisted of adding a new solids processing facility and the rehabilitation of the filter building to an administrative facility.

KENT R. McMANUS
Associate

EDUCATION

BS (Civil and Environmental Engineering) 1979; Clarkson College of Technology
MS (Environmental Engineering) 1980; Clarkson College of Technology

REGISTRATION

Professional Engineer

SUMMARY OF EXPERIENCE

Mr. McManus has been involved in a variety of environmental engineering projects. His experience includes solid and hazardous waste management, hydrogeologic investigations, physical-chemical treatment processes, sludge handling and disposal and industrial pretreatment.

DETAILED EXPERIENCE

1980 to Date — Malcolm Pirnie, Inc.

As Associate:

- Currently managing the hydrogeologic investigation and landfill design/permitting of the Phase II Area of the Chautauqua County Ellery Sanitary Landfill.
- Currently managing the hydrogeologic investigation and design of a sludge landfill expansion area for a confidential industrial client which involves a double composite liner system, leachate collection and on-site leachate storage, and quality assurance/quality control.
- Managed and prepared a Part 360 sludge land application permit renewal package for a confidential industrial client.
- Managing a solid waste project for a consortium of New York State paper industries which involves presenting justification for establishing a monofill classification with reduced liner requirements for paper industry wastes under 6NYCRR Part 360.
- Managed, supervised or prepared closure/post-closure plans and engineering evaluations for three municipal sanitary landfills and three industrial/private sanitary landfills. Supervised the preparation of a quality assurance/quality control plans for placement of soil cover systems.
- Prepared design concept and quality assurance/quality control (QA/QC) report for construction of an interim wide trench for disposal of industrial sludge for a confidential industrial client. Also supervised inspection and soil testing activities and prepared certification report which was subsequently approved by the NYSDEC.
- Managed, supervised or performed ten ground water/hydrogeologic investigations for industrial and municipal clients.

(over)

DETAILED EXPERIENCE (Continued)

1980 to Date Malcolm Pirnie, Inc. (continued)

As Project Engineer:

- Prepared closure/post-closure plans for two industrial hazardous waste landfills in Western New York including closure/post-closure cost estimates. Performing a detailed hydrologic/ hydrogeologic and pollutant transport evaluation for one hazardous waste landfill including installation of piezometers and lysimeters.
- Performed periodic inspection and prepared certification report for a hazardous waste container storage area which includes a synthetic membrane liner.
- Prepared an engineering report for a large power utility summarizing the hydrogeologic characteristics of the proposed location for an industrial landfill. Assisted the power utility in the preparation of a Part 360 Permit Application including review of design calculations and construction plans and specifications.
- Assisted a confidential NY client in attempting to obtain NYSDEC Part 360 permits to continue to operate an existing industrial landfill including: supervision of monitoring well installations, supervision of well sediment removal from existing wells, determination of in-situ soil permeabilities and preparation of engineering report.
- Developed conceptual designs and preliminary cost estimates for encapsulation of dioxin-contaminated, Love Canal related sewer and creek sediments. These conceptual designs were developed in accordance with current federal and state hazardous waste disposal regulations.
- Prepared a design certification report for installation of underground isopentane storage tanks for a confidential industrial client.
- Performed a hydrogeologic investigation of an existing industrial landfill for a confidential NY client including development of plan of study; design and inspection of soil borings and groundwater monitoring well installations; determination of in-situ soil permeabilities and preparation of engineering report.
- Prepared environmental assessment form, NYSDEC Part 360 construction and operating permits and the site development and closure plans for industrial landfill for a confidential NY client.
- Prepared NYSDEC Part 360 construction and operating permits, assisted in the development of an environmental impact statement and site development and closure plans for a sanitary landfill to dispose of sludge generated at the City of Niagara Falls combined industrial/municipal Wastewater Treatment Plant.

(continued)

DETAILED EXPERIENCE (Continued)

1980 to Date Malcolm Pirnie, Inc. (continued)

As Project Engineer: (continued)

- Assisted in the environmental assessment of a proposed sanitary landfill site for disposal of sludge generated at the Town of Amherst Municipal Wastewater Treatment Plant and prepared site development and closure plans.

MALCOLM PIRNIE

TERRY J. RIED
Project Engineer

EDUCATION

BT (Civil Engineering) 1978; Rochester Institute of Technology
AAS (Construction Technology) 1975; Erie Community College North
NYSDEC - Landfill Operator Course - 1986
Certified for Health and Safety Operations at Hazardous Materials Sites, April 1989

REGISTRATION

New York State Sewage Treatment Plant Operator - Grade IIA
Florida Sewage Treatment Operator - Class C

SUMMARY OF EXPERIENCE

Mr. Ried has more than 11 years of experience in the field of civil/environmental engineering. His experience in the solid waste field includes solid waste management, selection of sites for disposal facilities, hydrogeologic investigations, transfer station operation, recycling, landfill design, and landfill operation. Related experience includes wastewater plant design and operation, water and sewer main design and construction, storm sewer projects, and facilities planning.

DETAILED EXPERIENCE

1989 to Present Malcolm Pirnie, Inc.

- Responsible for the preparation of the detailed design documents (Plans, Specifications, Health and Safety Report, Wetland Permit Application, QA Report) of a cover system for a 6-acre industrial hazardous waste landfill for a confidential Western New York client. The project involves the design of a full RCRA-Guidance cap. The same project also includes the preparation of the detailed design for a Part 360 cover system for an adjacent 75-acre non-hazardous industrial landfill. Was also involved in the preparation of a revised closure plan and wetlands permit for this facility.
- Currently preparing the detailed design documents for a 25-acre industrial hazardous waste landfill in Western New York. Also prepared a revised closure/post-closure plan for the site.
- Assisted in the preparation of construction plans and specifications for the closure of a 12-acre construction and demolition debris landfill for the Village of Gowanda in Western New York.
- Currently working on the development of an office recycling program.

1987 - 1989 Manatee County, Florida

- Manager of County Solid Waste Division for a County with a population of 180,000.

(over)

DETAILED EXPERIENCE (Continued)

Manatee County, Florida (continued)

- Responsible for preparation, monitoring and control of $10 million annual operating budget and $5 million capital project budget.

- Responsible for waste collection in the County. Involved in solving field problems, coordinating activities of waste haulers, enforcement of mandatory solid waste collection ordinance, issuance of permits, processing service requests for approximately 53,000 commercial and residential customers and coordination of monthly billing activities.

- Prepared and reviewed engineering plans and acquired necessary permits regarding landfill operation. Involved 200-acre lateral expansion of existing landfill including stormwater system, leachate collection system, slurry wall design, monitoring well installation, soil borings and mitigation plans for existing wetlands. Also acquired permit modification for 75-foot vertical expansion on the active landfill.

- Responsible for daily operation of a 1000 ton/day, 150-acre sanitary landfill owned and operated by the County. Also responsible for post-closure activities of two closed landfills.

- Supervised 25 employees, developed and administered division policies and procedures, planned for future landfill projects.

- Initiated the development of a County recycling program to recycle aluminum cans, glass and newspaper through source separation. Project involved a phased approach beginning with five pilot-scale areas in the County. Also evaluated the potential for plastic recycling, office paper recycling and chipping of tires and wood waste at the landfill.

1985 - 1987 Cattaraugus County, New York

- Supervised County solid waste operations involving two landfills and nine waste transfer stations.

- Developed engineering reports, plans and specifications and acquired necessary permits to operate an 80 ton/day industrial waste landfill and a 20 ton/day construction and demolition debris landfill.

- Reviewed and approved necessary permits for waste entering landfills in addition to engineering plans and reports by consultants.

- Acted as County Liaison with regulatory agencies, other municipalities and engineering consultants regarding solid waste operations.

1980 - 1985 Edwards & Moncreiff, PC

- Project Engineer for the design and permitting of a new 70 ton/day County-operated sanitary landfill in Western New York. Included site selection process, hydrogeologic investigations, design of the landfill,

(over)

DETAILED EXPERIENCE (Continued)

Edwards & Moncreiff, PC

prepared plan of operation for the facility, preparation of construction plans and specifications, and all necessary permit responsibilities.

- Prepared an engineering report and design plans for operating permit renewal of a 5-acre construction and demolition debris landfill. Also, later prepared closure plan for same facility.

1979 - 1980 Malcolm Pirnie, Inc.

- Assisted in feasibility studies for two municipal sludge landfills, an industrial pretreatment study, and a stormwater contamination project at an industrial landfill.

MALCOLM PIRNIE

ANNE MARIE C. McMANUS
Project Engineer

EDUCATION

BS (Civil and Environmental Engineering) 1980; Clarkson College of Technology
MS (Environmental Engineering) 1981; Clarkson College of Technology
Solid Waste Landfill Course - University of Wisconsin Extension, March 1984

REGISTRATION

Professional Engineer

SUMMARY OF EXPERIENCE

Ms. McManus has been involved in a variety of environmental engineering projects. Her experience includes hazardous waste management, industrial pretreatment, and wastewater treatment process evaluation and design. Ms. McManus currently serves as the manager of Malcolm Pirnie's Soils Testing Laboratory.

DETAILED EXPERIENCE

1982 - Present Malcolm Pirnie, Inc.

- Currently managing a two-part study designed to provide data to the NYSDEC to justify paper industry wastes as a special classification of industrial waste (under NYCRR Part 360-2.14) with a resultant reduction in required landfill design requirements. Phase I consisted of characterization of the solid wastes generated by the paper industry and Phase II will review the effectiveness of an existing paper industry waste landfill with a single clay liner and evaluate the impact of actual paper industry leachate on clay liner material through a laboratory study.

- Supervised two laboratory column studies of the leachability of hazardous wastes as verification of a contaminant fate and transport model.

- Developed the laboratory procedure for the evaluation of the effects of landfill leachate on clay soils.

- Developed laboratory protocols for, and supervised testing of a number of alternative landfill cap or liner materials or mixtures.

- Developed the methodology for, and supervised a laboratory study to determine the effects of freeze/thaw cycles on landfill capping materials for a confidential client. Evaluated the effects of varying conditions of compaction, moisture content of the soil and number of freeze/thaw cycles. The results of the study supported a landfill cap design which did not include the standard NYSDEC-requirement of four feet of freeze/thaw protection in order to place the low permeability landfill cap beneath the frost penetration depth.

- Prepared construction certification reports for numerous landfill closures, including evaluation of soils characteristics and documentation of construction activities.

(over)

DETAILED EXPERIENCE (Continued)

Malcolm Pirnie, Inc. (continued)

- Assisted in the development of the plan of study to evaluate in-situ chemical treatment of PCB's in soil for a confidential client. Conducted the first field tests of the reagent, evaluated the results, and supervised a full-scale soil clean-up using the reagents.

- Performed an economic feasibility analysis of an industrial landfill for a confidential client which included preparation of a preliminary closure plan, review of previous hydrogeological work performed at the site and preparation of a proposal for Phase II site investigation.

- Performed site assessments and developed remedial programs for two PCB-contaminated sites under USEPA/NYSDEC Consent Order. Also performed an economic analysis for remediation of the sites including evaluation of excavation and secure burial of contaminated soils versus on-site containment and in-situ treatment.

- Prepared RCRA Part B Permit Applications for three confidential clients with hazardous waste container storage facilities, underground storage tanks, surface impoundments and land application facilities. These included review of the hydrogeologic conditions at the sites, preparation of groundwater quality assessment programs and preparation of recommendations to the industries for improved hazardous waste management practices.

- Assisted in the development of conceptual designs and preliminary cost estimates for encapsulation of dioxin-contaminated, Love Canal-related sewer and creek sediments. These conceptual designs were developed in accordance with current Federal and State hazardous waste disposal regulations.

- Performed a site investigation and an evaluation of remedial alternatives for a confidential industrial client to identify the source of volatile organics contamination in a storm sewer outfall. The investigation consisted of a sewer sampling program, sewer televising, a soil gas survey, and hydrogeologic investigation.

- Evaluated the alternatives for remediation of a PCB-contaminated wastewater sludge for a confidential industrial client. Remedial alternatives evaluated included sewer cleaning, improved sludge management operations to reduce the volume of sludge to be disposed of, and improved operation of the wastewater treatment facilities for better solids separation.

- Performed a feasibility study for the Vestal, New York Federal Superfund Site which consisted of a municipal water supply well contaminated with VOC's. The alternatives which were evaluated included: continuing to pump the well to waste to contain the plume of contamination; GAC and/or air stripping of the well water; installating an interceptor well to contain the plume; or developing alternative water supplies.

(continued)

DETAILED EXPERIENCE (Continued)

Malcolm Pirnie, Inc. (continued)

- Prepared the conceptual design and cost estimate for replacement of out-dated underground steel storage tanks for a confidential industrial client. The tanks were replaced with double-walled steel tanks with leak detection, cathodic protection, level inventory monitoring and double-walled piping to meet current standards for petroleum storage facilities. The conceptual design also included a rail car unloading spill containment pad and closure of the existing steel tanks in accordance with NYSDEC guidelines.
- Performed a site investigation of an orthochlorotoluene spill at a major oil storage facility. The investigation included a soil gas survey, installation of soil borings and groundwater monitoring wells sized for spill recovery and pump testing to determine the hydraulic conductivity of the underlying soils.

APPENDIX 4-A

SITE INSPECTION CHECKLIST AND MAINTENANCE SCHEDULE

SITE INSPECTION CHECKLIST

Date:

Inspected By:

	CONDITION: (Check)				
	Acceptable	Not Acceptable	Present	Not Present	REMARKS
1) Vegetative Cover					
a) Landfill Site	___	___			
b) Mining Area	___	___			
c) Drainage Ditches	___	___			
d) Leachate Collection System	___	___			
2) Integrity of Drainage Ditches					
a) sediment build-up	___	___			
b) pooling or ponding	___	___			
c) slope integrity	___	___			
d) overall adequacy	___	___			
e) anti-erosion matting	___	___			
f) lining	___	___			
3) Integrity of Gas Vents	___	___			
4) Condition of Access Road					
a) road condition	___	___			
b) gates/locks	___	___			
5) Integrity of Groundwater Monitoring Wells	___	___			
6) Integrity of Landfill Cap					
a) erosion damage			___	___	
b) leachate breakthrough			___	___	
c) settlement			___	___	
d) cracking			___	___	

SITE INSPECTION CHECKLIST - continued

Date:

Inspected By:

	CONDITION: (Check)				
	Acceptable	Not Acceptable	Present	Not Present	REMARKS
7) Leachate Collection System					
a) flow in pipe	___	___			
b) sediment in pipe			___	___	
c) storage tank - structural integrity	___	___			
d) high water level in leachate storage tank			___	___	
8) Other (e.g. litter, unauthorized dumping, etc.					

MAINTENANCE SCHEDULE

Date:

MAINTENANCE PERFORMED (check) — ITEM — REMARKS

___ 1) Vegetative Cover:
___ a) seeding
___ b) fertilizing
___ c) topsoil replaced
___ d) removal of undesirable vegetation

2) Drainage Ditches:
___ a) excavation
___ b) landfill cap replacement
___ c) fill
___ d) regrading
___ e) vegetative cover placement
___ f) stone lining replacement
___ g) anti-erosion matting replacement

3) Leachate Collection System
___ a) collection pipe flushing
___ b) sediment removal
c) repair/replacement:
___ i) collection piping
___ ii) excavation
___ iii) gravel backfill
___ iv) non-woven filter fabric
___ v) fill/cover
___ vi) vegetative cover
___ vii) storage tank

4) Access Road
___ a) fill
___ b) grading
c) Repair/Replacement:
___ i) gate
___ ii) locks
___ iii) signs

MAINTENANCE SCHEDULE - continued

Date:

MAINTENANCE PERFORMED (check)	ITEM	REMARKS
	5) Repair/Replacement:	
	a) Gas Vents	
___	i) excavation	
___	ii) gravel fill	
___	iii) vent pipe	
___	iv) screen	
___	v) cover	
___	vi) vegetative cover	
	b) Landfill Cap	
___	i) excavation	
___	ii) cover	
___	iii) compaction	
___	iv) testing	
___	v) grading	
___	vi) vegetative cover	
	c) Groundwater Monitoring Wells	
___	i) drilling	
___	ii) screening	
___	iii) casing	
___	iv) pipe	
___	v) fill/grout	
___	vi) cap	