

barrier (6). This secondary bond type has intermediate reversibility depending on the temperature and may even exhibit syneresis, as in the development of after-tack.

This brings us to the third type in which the structural units do not have to be pre-formed but are the system itself. Here cross linkage and rapid film formation is due solely to secondary valence bonding. Two cases may be considered, a) where the secondary bonding is weak, 500 calories, and b) where it is strong, 5,000 calories per atom or atom group. With respect to the first I prepared some years ago pseudo oil ink films which dried to touch in a moment or two but were repeatedly reversible to the sol stage merely by agitation at room temperature (7). In these films the secondary valence bonding is of course quite weak. The styrenated alkyds which belong to the second type also undergo film formation promptly in accordance with the facile orientation and secondary bonding of the inherent structural units of the system. The secondary bonding is quite strong, and the films have a considerable degree of irreversibility at ordinary temperatures. Of course being a drying oil system, the styrenated alkyds subsequently continue to oxidize and harden further.

As is quite apparent the split second film formation obtained with the styrenated alkyds brings the drying oils for the first time within the scope of the high speed printing operations previously discussed. From this point on it becomes an economic question as to whether this new approach to drying oil film formation can compete in price and qualities with the currently used rapid methods of evaporation and phase displacement. The styrenated alkyds now on

the market require aromatic solvents as the thinner which limits their use to gravure printing. Another limitation is their rather strong odor, caused by unreacted styrene monomer, which is a decided drawback in the food packaging field. The odor will have to be eliminated before serious commercial consideration can be given to this interesting material. Notwithstanding their present limitations, the styrenated alkyds and other drying oil adducts which film-form by a similar mechanism offer one possibility as to the way out of the present dilemma of the drying oils in the printing ink industry.

Conclusion

An analysis has been made of the historical position of the drying oils in the printing ink industry, of their current curtailed usage, and of the performance requirements of drying speed and minimized odor which have contributed to this curtailment. The situation from the long-range viewpoint is a serious one. It is a challenge and opportunity alike for the oil chemist to understand in a fundamental sense the physics and chemistry to the process of film formation of the drying oils. The styrenated alkyds and the bisphenol-epichlorhydrin esters point the way to the concept of film formation of drying oil systems in which oxidation is not the dominant factor.

REFERENCES

1. Bernstein, I. M., *American Ink Maker*, 26, 33 (1948).
2. Long, J. S., *Jour. Oil & Colour Chemists' Asso.*, 32, 377 (1949).
3. Bowles, R. F., *Jour. Oil & Colour Chemists' Asso.*, 33, 97 (1950).
4. Mattiello, J. J., and Work, L. T., *Nat'l Paint, Varnish, Lacquer Asso. Circ.*, 31, 502 (1936).
5. Bernstein, I. M., *Jour. Phys. & Colloid Chem.*, 52, 613 (1948).
6. "Physical Chemistry of High Polymeric Systems," p. 92, H. Mark, Interscience Publ., N. Y. (1940).
7. Bernstein, I. M., unpublished data.

Miscellaneous Uses of Drying Oils

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OILS consumed under the categorical heading of "miscellaneous uses" have been growing in considerable volume. The Bureau of Census reported 93,000,000 pounds consumed in 1943; this quantity increased steadily to 180,000,000 pounds in 1948. These miscellaneous uses of drying oils are diversified and cover a wide latitude of application.

Grouped in this classification are all the end uses of drying oils not covered by paints, varnishes, resins, linoleum, and printing inks. The facets of the uses are so numerous that a paper such as this must, of necessity, be limited. Generally, miscellaneous uses cover all the oil consumed in putty, mastic, caulking and deadening compounds, insulating material, rubber, rubber-like compounds and coated fabrics, core oils, stamping and draw-

ing compounds, rustproofing agents, slushing and metal tempering oil, binders for brake blocks and fibre gaskets, stiffening agents for pressed wood hardboard operations, petroleum additives for pneumatic tool and steel cylinder stock lubricants, fluxes for tin and terne plate, textile sizes, roofing compounds, leather treatment, wood treating chemicals; pharmaceuticals, toilet articles, disinfectants, detergents, insecticides, fungicides, etc. Most of those enumerated above will be treated to a lesser or greater degree in this paper as the demand may require or the information covering is available.

Caulking Compounds. Of all the miscellaneous uses of drying oils those used in the manufacture of putty, glazing, and caulking compounds are familiar to coating manufacturers to about the same degree as paints. There is a relation between caulking, glazing compounds, and putties, since all are "over-pigmented vehicle plastic bases" and may in many cases be used interchangeably.

The function of caulking compounds is to fill joints between wood and wood, wood and masonry, metal and masonry, or between masonry and masonry. Caulking compounds are available in three grades, gun grade, knife grade, and cord. Sometimes the last type is



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referred to as "Calk-Cord." The gun grade is the least viscous of the three while the "Calk-Cord" is a firm plastic material, and the knife grade is intermediate between these two grades. Irrespective of the grade caulking compounds must perform as follows:

1. must not sag
2. must have controlled shrinkage
3. must not stain
4. must adhere to the surface
5. must not be thermosensitive, to prevent sagging under higher temperatures
6. must be fairly chemically resistant and weather resistant
7. must be impervious to water and water vapors
8. must form a skin in 24 hours over the plastic mass
9. must have color stability
10. must have package stability; the bulk of material must maintain its softness and not become too rigid even after a skin forms

Caulking compounds may be made in most heavy mixing machinery such as a dough mixer, Baker-Perkins and lead mixers.

The vehicles generally employed in manufacturing caulking compounds are linseed oil, fish oil, soybean oil, castor oil, and small amounts of tallow. Some vehicles may even contain tall oil, mineral oil, and chemical plasticizers. In using the modifiers, bleeding and discoloration must be carefully controlled. The use of thinners is not precluded provided shrinkage and staining is kept to a minimum.

Pigments used in the manufacture of caulking compounds are asbestine, asbestine shorts, asbestine floats, whiting, marble dust, and hiding pigments such as TiO_2 , white lead, lampblack, iron oxides, etc. Generally if hiding pigments are used, the practice is to add them before the addition of the extenders. Since the formation of a skin is desired, the incorporation of soluble driers is deemed practical.

Knife Grade Caulking Compound

Calcium Carbonate.....	1250
Asbestos Fibre 7 M.....	150
Basic Carbonate White Lead.....	100
Bodied Fish Oil.....	320

Gun Grade Caulking Compound

Asbestine 3 X.....	390
Asbestos Shorts 7 M.....	195
Soluble Bodied Fish Oil (76% non-volatile).....	545
6% Cobalt Naphthenate.....	3

Glazing Compounds. These are similar to caulking compounds and putties. The similarity to caulking compounds ceases after comparisons are made in respect to body and to drying. Glazing compounds are similar in body to caulking compounds, and a skin forms on drying. These properties are a compromise as a result of the requirements.

Glazing compounds are generally used on metal sashes, either iron or aluminum, to hold the lights in place. The window must be anchored firmly yet the glazing compound must have some resiliency to overcome the expansion and contraction of the metal. For that reason a compromise in plasticity is made between the more plastic caulking compounds and the less plastic putty. Oils and pigments used for the manufacture of caulking compounds may be used also. In aluminum glazing compounds aluminum powder of the paint grade is generally added.

Glazing Compound

Refined Soya.....	92
680 vis. Blown Soya.....	9
Commercial Whiting.....	204
Dry Ground Whiting.....	124
Marble Dust, 85% 200 mesh.....	102
3 X Asbestine.....	24
7 M Asbestos Shorts.....	15

Aluminum Glazing Compound

Alkali Refined Fish Oil.....	90
Bodied Fish Oil.....	10
Commercial Whiting.....	205
Marble Dust 85% 200 mesh.....	105
Limestone, dry ground.....	120
3 X Asbestine.....	24
7 M Asbestos Shorts.....	15
Standard Aluminum Powder.....	20

Putties. The function of putties is to fill general irregularities, mainly on wood. Such irregularities may be imperfections of natural causes such as cracks, specks, etc., or man-made causes, such as nail holes. While putties may be used in the same places as caulking and glazing compounds, the prime use of putties however is to hold lights firmly into wooden sashes. Since the expansion and contraction of wood is practically nil compared with metal sash in temperature changes, the properties of caulking or glazing compounds are materially different. The main difference is that no skin formation with a softer interior is needed in putty compounds, but a firm thoroughly hard, non-skinning product is necessary. Putties are applied by hand and a putty knife. Therefore it is necessary to make a putty that has minimum stickiness to prevent the bothersome adherence to hands, and secondly, on knifing, the putty should finish off with an even glossy effect.

Putties may be made from either low or high acid number linseed oils. However where high percentages of pigment are needed, a fairly high acid number raw linseed oil should be used. Where label requirements are not stringent, other drying oils may be used. Most putties are made from whiting, chalk, etc., although some are known to contain white lead and/or red lead, etc. Generally, equipment necessary to manufacture caulking or glazing compounds may be used, but the lead chaser is still considered the orthodox method of manufacture.

Commercial Putty

Whiting.....	600
Raw Linseed Oil.....	100

White Lead Putty

Basic Lead Carbonate.....	155
Whiting.....	1425
Linseed Putty Oil, Acid No. 20.....	250

Rust Proofing Agents. The formulating of rust-proofing agents will vary considerably with the requirements demanded of these compounds. The length of time the metal is to be subjected to the weather, the type of application (spray, dip or brush), and the cost are the principal considerations. All of these compounds have two requirements in common: the ability to rustproof and the ability to remove easily from the metal surface.

Cheap compounds are based on petroleum oils and greases, which have poor rustproofing qualities and are difficult to remove. Better products contain blown fish oils, degreas, and other semi-drying oils. In gen-

eral, products which will withstand a five-minute period under a hot water faucet tap and still remain intact, be capable of removal with a caustic water bath or solvent, and be non-corrosive to metal are considered most satisfactory.

Some rustproofing compounds are required to "dry at room temperature for 24 hours;" not crack when bent around a one-quarter inch rod at -40°F .; be sufficiently dry after 24 hours to permit handling without injury to the coating; pass a 10-day salt water spray test; a 30-day humidity and ultra-violet ray test; and be completely removable with "dry cleaners' solvent."

Many rustproofing specifications will not permit the use of rosin or chromates. United States Army Ordnance Specification 2-84B is included in these. The Ordnance Department AXS 673 rustproofing specification must pass the most rigid requirements at a maximum film thickness of .008 inch thick and still be removable with kerosene.

A very few rustproofing compounds are not expected to be removed. One of these is a pigmented type covered by the Bureau of Ships 52 C 17 for use on submarine ballast tanks and steel decking. This type does not use drying oil and does require rosin and chromates, quite in the reverse of most specifications.

Navy Specification 52 C 18 covers three grades of thin film rustproofing compounds which should withstand two to four weeks' salt spray test and be removable with wiping cloths saturated in kerosene. In general, most rustproofing compounds are not permanent coatings and must be removable. The surface of the metal should then be sufficiently clean for painting purposes.

Certain chemical additives are frequently used to increase penetration. Some of these additives are used on surfaces already rusted so that the compound will penetrate the rust and secure it to the surface. These materials consist of "lead soaps" or "drip gas oil."

Soluble chromates are also used for rustproofing agents. These are basic and neutralize carbonic acid formations which would accelerate rusting. Sperm oil which contains approximately 30% cetyl alcohol is said to have excellent penetration characteristics and is frequently used in rustproofing compounds. A typical low cost rustproofing compound would be formulated as follows:

40 parts blown fish oil Z-5
10 parts degrass
5 parts rosin
2 parts lead linoleate
43 parts V. M. & P. naphtha

Stamping and Drawing Compounds. Special soaps and lubricants are required in the stamping of metal objects such as auto headlights, hub caps, and the numerous metal parts designed to various shapes. These lubricants are also required in drawing wire, aluminum and brass pipes, etc.

Vegetable and marine oils are used in these compounds for definite purposes. The blown fatty oils have a much greater tenacity or resistance to shearing than petroleum greases. They will adhere to a metal surface under the high temperatures developed during the stamping operation and not "pull away" from heat as a petroleum oil will. They can be removed economically in a caustic bath by saponification, rather than by expensive solvent degreasing

processes. The surface of the metal is "cleaner" from the standpoint of painting or plating than is possible with petroleum greases.

Frequently the stamped metal object is stored "out of doors" and subjected to the weather for a period of time. In this case the stamping compound is also expected to act as a rustproofing agent in protecting the metal. Semi-drying oils will "set up" and form a tough coating that can still be removed by saponification. Petroleum greases have far less value as a rustproofing agent.

In spite of all the desirable characteristics of blown fatty oils in stamping compounds, these are still more expensive than petroleum products, and for economic reasons compounds containing both mineral oil products and blown fatty oils are generally used.

Approximately 20% of saponifiable oil is necessary to provide minimum requirements for tenacity, adhesion, and cleansing properties in a low-cost stamping compound. Such a product could be formulated as follows:

8% soap (oleic acid, tallow, fish oil)
12% blown fish oil Z-6
80% mineral oil

Limed fatty oil soaps are used for drawing wire, aluminum, brass, or copper pipe. These compounds are based almost entirely on fatty oils since this type of processing involves considerably higher temperatures and pressures. Blown fish oils are compounded with lime to form a tough "soap" required in the lubrication of drawing these metal objects.

Pneumatic Tool and Steam Cylinder Stock Lubricants. Special lubricants are required for pneumatic tools, air compressor cylinders, steam cylinders, and reciprocating steam engines. These usually contain from 2% to 20% "fixed oils." The approved fixed oils are blown rapeseed, tallow, lard, mustardseed, peanut, or fish oils.

Equipment subjected to steam, or air containing moisture is best lubricated with oils having emulsifiable properties. Since mineral oil is lighter than water, metal surfaces would "spot rust" if this compounded lubricant were not used. Inland equipment such as locomotive cranes, steam hoists, and steam shovels require this lubricant as well as most marine equipment.

The "fixed" saponifiable oils used generally have a viscosity of 500-720 Saybolt at 210°F . They are blown to increase emulsifiable properties and should contain a minimum of free fatty acids, no moisture or gumming constituents, and be miscible with certain petroleum oils. Generally, Texas asphaltic or mid-continent petroleum oils are used. The Pennsylvania paraffinic types are not used because of their incompatibility with blown fatty oils. These "fixed" oils are usually blown at a high temperature to increase solubility characteristics and are generally dark in color. They are expected to be completely soluble in the mineral oil used and not settle out on standing for prolonged periods.

Steam emulsion tests and demulsification tests are carefully run in evaluating this type of lubricant. These tests are covered by "Federal Standard Stock Catalog VV-L-791" and A.S.T.M. procedures. The steam emulsion number is reported as the SE number. Rapeseed oil was once used almost exclusively in this type application. However rapeseed is imported from Manchuria and is subject to a tariff. Domestic

oil such as fish and peanut are much lower in cost and equally suitable. These latter oils have been approved for use by the Navy and industrial compounders during the last war.

Special oil and gasoline resistant greases requiring the use of vegetable and fish oils are covered by Army-Navy Specification AN-G-14. These gasoline resistant greases are used on gaskets and taper plug valves employed in the fuel and air systems of aircraft. These greases should be not more than 10% soluble in a mixture of aviation gasoline, toluene, xylene, and benzene. The greases are composed of vegetable or fish oil compounded with a sodium or potassium fatty oil soap. This is a dry soap, relatively free from water. The soap content is approximately 20% of the total grease.

Core Oils. A core oil is used as a binder for sand in forming the core of the mold in which metal castings are made. The oils used for this purpose are linseed, soya, chinawood, oiticica, and tall oil. Frequently petroleum polymers, cereal binders, rosin, and other resins are used to decrease costs and increase the "green strength" of the core. The term "green strength" applies to the rigidity of the core before baking and denotes the ability of the core to withstand handling.

Rosin, tall oil, and similar thermoplastic materials are excellent binders but will soften when the hot metal is cast, causing a warping or sagging of the core. Oxidizing oils such as linseed, soya, and wood oil will not soften under heat and do increase the rigidity of the core during casting operations.

Cores are baked at various temperatures, depending on the equipment used at each particular foundry. Some foundries bake cores over-night over a coal fire with little regard for temperature control. Others are more careful to obtain maximum core strength by following a regular baking cycle.

A good core oil is expected to reach a maximum strength in three to four hours' bake at 425°F. Suppliers recommend about four hours at 400°F. The core should support molten metal without softening or warping until the metal has "set," and then the core is expected to burn up or disintegrate so that it may easily be removed from the casting. This is extremely important in casting thin one-quarter inch steam radiator tubes from which the burnt-out sand core must flow. If the core remained rigid, it could not be removed and the core would be rejected.

A typical core oil has a viscosity of A-G and from 65% to 100% solids. No drier is used as this would cause the sand/oil mix to "set up" on the core bench. The core oil is also required to provide proper "feel" and "lubricity" to the sand so that the sand core may be molded properly and not stick to the core box.

One part core oil to seventy to a hundred parts sand is usually used. A typical core oil may be formulated as follows:

Esterified refined tall oil.....	20%
Raw linseed oil.....	70%
Low viscosity mineral oil.....	10%

Tin and Terne Plating. Palm oil up to the present time has been a strategic material in the manufacture of tin and terne plated steel (1). In hot dip tinning, clean steel sheets are carried by rolls through a flux

of zinc chloride solution into a bath of molten tin and up through an 18-inch layer of hot palm oil. Both the flux and the palm oil float on the surface of the molten tin in their respective boxes. Three sets of adjustable steel rollers are generally used to smooth the film of tin. After coating, the tin plate passes through a felt or canvas roller over which wheat bran is distributed. This cleans off excess oil and imparts the bright look which is so attractive.

Tin of commerce is essentially pure, approximately 99.8%, with a melting point of 232°C., necessitating the use of an oil that at a cracking temperature of 240-290°C. must not volatilize rapidly, must not polymerize and become "sticky," and must clean rapidly from the sheets. Yet a small amount of heat degradation is necessary since these products help to remove the oxides and wet the metal properly.

Without the oil, the tin coat would be uneven and the surface would become powdery as the tin oxidizes when exposed to the air at the high heat. A good oil for tinning must be stable as well as non-inflammable at working temperatures, must pour at room temperature, be non-toxic, odor-free, and cheap; must not interfere with lithographing, lacquering, or soldering; and must be plentiful and economical. Palm oil meets all these requirements although hydrogenated oils have been used. However during the last war our source of palm oil from the Far East was cut off, curtailing the production of cans for food packaging, necessitating a research program to find another oil to make our tin plate industry as self-sufficient as possible.

An oil is now being tested in production that is prepared from dimerized linoleic acid combined with methyl dimerate. This oil is not as volatile and does not become too viscous as does palm oil.

Chemicals Derived from Drying Oils. The use of drying oils or unsaturated acids derived from drying oils, for production of chemicals, does not compare in scope with the amount of materials prepared from hardened or naturally occurring saturated oils because of the difficulty experienced in handling the unsaturated material as well as the economics involved. However, unsaturated compounds do find their use in industry.

By the complete breakage of double bonds in linoleic acid without oxidation of the primary products we should produce caproic, malonic, and azelaic acids. Linolenic acid under the same conditions should produce propionic acid, azelaic, and two moles of malonic acid. If the acid contains a conjugated system of double bonds, we should expect, for instance, from elaeosteric acid, valeric acid, azelaic acid, and two moles of oxalic acid. However the above primary oxidation products are not always obtained, partly due to the fact that a quantitative break seldom occurs and the primary product may be partly or completely oxidized to a lower molecular weight acid (2).

If partial oxidation of the double bonds occurs, we obtain products such as di and polyhydroxy, hydroxyketo, diketo, and oxide acids. For example, the partial oxidation of linoleic acid furnishes us tetrahydroxy stearic acid and the partial oxidation of linolenic acid forms a hexahydroxystearic acid. These partial oxidation products are obtained by the use of cold dilute alkaline permanganate (2). These products have found a place in the manufacture of plasticizers, softeners, and starting points for other derivatives.

The first synthetic detergent, dating back more than a hundred years, was the sulphuric acid derivatives of vegetable oils. Shortly after the First World War the I. G. Farbenindustries developed Igepon A, which is a sulfonated fatty acid ester. The study of its detergent properties led to the realization that the carboxyl group inhibited detergent action, leading to the manufacture of fatty alcohol sulfates. The manufacture of the fatty alcohol sulphate required fatty alcohols, the manufacture of which was first started in 1933 by E. I. duPont de Nemours Company Inc. at Deepwater, N. J., using a sodium reduction process. Although a German operation started in 1928 for the manufacture of fatty alcohols used high pressure hydrogenation, the duPont Company used the sodium reduction process because it permits the production of unsaturated alcohols. The German process attacks the unsaturated bonds before the ester group is reduced, resulting in a saturated alcohol, whereas the sodium reduction seldom affects unsaturation although certain conjugation systems may be rearranged. While today the major market for fatty alcohols is in the manufacture of synthetic detergents, it is believed that the esterification of these products with dibasic acids to form plasticizers will some day be a new market (3).

A new field of chemicals, based upon fatty acids, has been developed since 1935, for the production of amides, nitriles, amine acetates, and quaternary ammonium salts. While the bulk of these materials are prepared from saturated or hardened acids, soybean oil, as well as other semi-drying oils, can be utilized in their preparation.

Fatty acids react with ammonia to form amides which at elevated temperatures over an aluminum oxide catalyst are dehydrated to form the corresponding nitriles. Nitriles can be hydrogenated to primary amines at a pressure of 200 pounds per square inch of hydrogen at 150°C., using Raney nickel as the catalyst. Nitriles may also be reduced to secondary and tertiary amines by the use of a higher temperature and more effective catalyst. The amine acetates are prepared by pumping together through proportionated pumps, acetic acid and the amine, the mixture stirred and cooled to remove the heat of reaction. The quaternary ammonium salts are prepared by the treatment of the amine with methyl chloride. These four chemicals find a use as tack reducing agents in rubber and resin coating, mutual solvents for waxes and resins, water repellents, softening agents, lubricants, dyeing assistants, and the synthesis of other compounds (4).

Medicinal Oils. The use of castor oil for medicinal purposes has been general but not too enthusiastic. While castor oil is not considered to be a drying oil, it certainly fits into the picture on the use of miscellaneous drying oils since it is the daddy of dehydrated castor oil. Criticism due to commission is slightly more tenable than that received from omission. For that reason cashew nutshell liquid is included as a miscellaneous drying oil. Actually, the reason is more feasible if one realizes the use of modified cashew nutshell oil in the protective coating and insulating varnish end of the paint industry.

Cashew nutshell oil contains a phenolic compound called "Cardol" ($C_{32}H_{52}O_4$) and an acid $C_{22}H_{32}O_3$ called anacardic acid. The oil has medicinal value for warts, corns, ringworm, and cancerous ulcers. It

is applied to the soles of the feet to prevent cracking of the cuticle and is an anesthetic in leprosy cases (5).

Linseed oil is suitable for both internal and external medicinal use. Alone or with lime water, it is used for the relief of superficial burns. It also is used in enemas, especially in hemorrhoid cases. A solution of linseed oil and sulfur was formerly used in treatment of scabies and parasitic skin diseases.

The work of Burr and his co-workers on the deficiency disease caused by the lack of linoleic, linolenic, and arachidonic acids in feeding tests showed that the animal organism definitely requires these essential unsaturated acids and yet lacked a mechanism for synthesis from carbohydrates and was not able to produce them by dehydrogenation from ingested or stored fats. However these acids are so readily distributed in nature that a deficiency of this acid in a normal diet is a rarity.

Vitamin Oils. These are included here since they may have a common source as the miscellaneous oil.

Vitamin A — Anti-xerophthalmic — occurring most abundantly in oil from the liver of halibut, cod, and other fish. It is also being prepared synthetically.

Vitamin D₂—Natural antirachitic portion of fish-liver oil.

Vitamin E—X-tocopherol—anti-sterility vitamin. The best natural sources are wheat germ and cottonseed oil.

Insecticides. The use of glyceride oils in insecticides is to obtain a blending or adhesive medium for insecticides, an adherent to the plant, maintenance of the mixture over a reasonable length of time during dry and wet weather, etc., good coverage of spray, and slow drying to prevent hard film formation so that the oil is liquid to 40°F. Four systems for the use of oil are as follows:

- a) in combination with kerosene
- b) as a sulfurized oil mainly sulfur and fish oil combinations
- c) as a soap to prepare water solutions
- d) as a stick adhesive in tree banding compounds

The oil in the last use is formulated with a non-drying sticky constituent, or a drying modifier for the oil such as a B naphthol. A typical tree banding over paper consists of:

- 1 part rubber latex
- ½ part fish oil
- 15 parts mineral oil
- ½ part rosin
- 1 part sweetening material

Cashew nutshell liquid is an accepted repellent for white ants and insects (5).

Leather Treatment. Compounded oils used for treating leather for the soles of shoes are the semi-drying type having iodine values of 120-150. U. S. Army Specification 92-62 covers two types, both of which have 60% non-volatile oil and 40% solvent. Type A should contain a minimum of 25% blown fatty oil while Type B contains 95% blown fatty oil. Another specification for compound for leather treating is JAN-C-1063. The blown oil used in this type specification is 550 Saybolt at 130°F. and consists of low iodine fish oil, herring oil, or other suitable semi-drying oil. The balance of non-volatile oil can consist of mineral oil.

This leather treatment increases water resistance, resistance to wear and scuffing, and in general will prolong the life of the leather. Petroleum oils tend to

"dry out" and do not contribute in the same manner as the oil more closely approximating that contained in the original hide. A typical oil consists of 50 parts of blown fish oil and 15 parts of common Degras which are heated and stirred. To this is added slowly 10 parts of water containing a good wetting agent.

Oils used in belt dressing are intended to increase the "grip" or friction that exists between belt and pulley. These oils should penetrate the belt and increase flexibility while at the same time providing a water and chemical resistant coating. A combination of light kettle bodied fish oil, degreas and paraffin oil will make a suitable belt dressing. Solvents are not used due to the fire hazard involved.

Rubber, Rubber Tile, and Factice Compounds. White factice is a light colored, compressible material, principally used as an extender or modifier for rubber. A large volume of this material is used in the manufacture of erasers. The method of manufacture is to react a semi-drying oil with sulfur monochloride at room temperatures.

Brown factice, an unsaturated oil, is reacted with sulfur at its melting point. Blown oils are quite generally used. By varying the processing and ratio of oil to sulfur a viscous dark liquid, a hard solid is produced. The material finds usage as a rubber extender, manufacture of linoleum, etc.

A recent development, a product quite similar to natural rubber, is made by obtaining the dimerized fatty acids from a Y bodied soybean oil. These are made by saponification acidification of the bodied oil and distilling off the dimerized acids. The acids are then neutralized with ethylene glycol. The ester has been used for the manufacture of rubber gaskets, tubing, etc.

Pressedwood Fibre Boards. Stiffening and tempering oils are used in pressed fibre hardboard operations to increase the strength of the board. Frequently these boards are used for masonry forms, and the impregnation with drying oils also increases the water absorption resistance and alkali resistance.

Several methods are used in tempering hardboard. In one method the finished board is immersed in an oil mixture for three to 10 seconds, during which 6 to 9% oil by weight of the board is absorbed. The board is then baked for three to six hours at 300°F. This treatment will increase the modulus of rupture from 800 PSI in the untreated board to 1,500 PSI.

A second, a west coast process, consists of blending an oil, resin, and wax combination with damp wood fibre in a cyclone mixer. An eight-inch thick felt mat is made, which is then hydraulically pressed while heat is applied at the same time, fusing the binder and wood film together.

A typical tempering oil for hardboard may consist of 50% drying vegetable or marine oil and 50% petroleum polymers. Small quantities of driers are used to insure proper bake. These oils should be 95-100% solids and have a viscosity not exceeding H-I. The quantity of oil absorbed by the board can be controlled by viscosity, temperature of the oil bath, and length of immersion period.

Automotive Gaskets. Thin asbestos sheets are first roller coated with a liquid fish oil/graphite mixture. These sheets are coated on each side and cut to a size suitable for use on the gasket forming machine.

The sheets are stacked about two feet high and placed in rows for "curing." Heat develops in the

stack of asbestos sheets, which causes the oil to harden, or sheets of the treated asbestos are placed on either side of a copper gasket frame and are laminated by machine operation.

Brake Block and Brake Linings. Originally, binders consisted of pitches, as saturants for woven lining; later blends of pitches and drying oils, also as woven lining saturants, cured by heat and oxidation. Later these blends were used as binders for molded segments. Of later years they were bodied and employed as such with sulfur as the binder. When thus employed, they produced molded linings of type capable of being produced in rolls and quite flexible.

With increase in vehicle weight and higher speeds, together with requirements for improved brakes, oils have been substituted in part by phenolic resins, either in the form of mixtures, in which case sulfur is employed, or as an oil-modified phenolic resin containing from 15 to 60% vegetable drying oil. Such binders are used with and without sulfur. The oils most commonly employed are linseed, dehydrated castor, or wood oil. Today most impregnants for woven linings contain an appreciable percentage of vegetable drying oil.

Oils have a characteristic of imparting softness to friction elements when used as the modifier for phenolic resin binders and thus reduce scoring tendency and prevent loss of friction from glazing commonly characteristic of unmodified phenolic binders. Very often, the oil is reacted directly with the phenolic resin in the process of manufacture of the latter and exhibits in many instances unusual resistance to breakdown by heat.

Chinawood oil alkyds have been used, but, in fact, these are considered of no value today.

Textile Printing and Dyeing. The use of oil modified alkyds is playing a predominant part in this industry. Generally, an emulsification is carried on in the presence of an organic solvent. The emulsions may be of two types, either water and oil, or oil and water. Pigments and dyes are generally added. These pigments are dispersed in organic resins; sometimes flush colors are used. These materials are used for rayons, cotton goods, and other materials in the textile trade.

Textile Coating and Artificial Leather. Considerable quantities of blown soybean oil have been used in manufacture of textile coatings and artificial leather. However, currently, this has been supplanted to a large extent by the use of vinyl compounds.

Wood Treatment. A typical wood treating compound, sealer-wood preservative, is described in U. S. Army Specification 3-186. This specification involves the use of linseed oil, alkyd base, and oil resin base with the use of various fungicides, such as pentachlorophenol, phenol mercury salts, and others. However, for industrial use, fungicides may not be present although it is common practice now to add some fungicides to commercial wood treating compounds, and they differ very little from the government specification material. Since the purpose for commercial use is to prepare a finish for wood such as gun stocks, which would be subjected to marring on handling, the specification is slightly different. There is a U. S. Army Specification 3-216 describing such a material.

Generally speaking for the latter, a chinawood and linseed oil penetrating combination is made and a penetrating solvent is customarily used with these

oils, as creosote or high flash naphtha. Since the penetration fills the interstices in the wood, the wood is kept lively, and since no surface coat is applied, any marring incurred can be more easily doctored.

Paper Coatings. Very little information is available on the use of drying and semi-drying oils in paper conversion work although paper for stencilling machines has been impregnated with either linseed oil or soyabean oil modified alkyds. Cap liner papers have been prepared from varnishes, but this practice has been largely supplanted by vinyl coatings.

Insulating varnishes. A resumé of the varnished insulations in electrical engineering by David O. Woodbury and published by the National Electric Manufacturers Association of 155 East 44th street, New York 17, N. Y., is an excellent reference book on the use of insulating varnishes. Insulating varnishes are of two types, impregnating and coating types. Exact formulations are not available, but, in general, drying oils are used extensively in insulating varnishes. The desirable qualities of both types are as follows: Resistance to heat at elevated temperatures, power factor, di-electric strength, and flexibility. Flexibility properties for impregnating varnishes are not as high as the coating type. The impregnating type however must have deep dry properties.

The predominant oil used in insulating varnishes is chinawood oil. Other oils are also used extensively in that type of varnish, the kind depending on the properties of the particular varnish desired. Heat resistance and things like that are affected by the oils used. The oils must be modified to suit the particular requirements. Ureas, melamines, and phenolics are used as modifiers.

Varnishes are applied to fabrics, cotton, or paper based on rag, hemp, rope, or Kraft and quite frequently on asbestos where high temperature duty is desired. Varnished fabrics must meet the following requirements:

- a) di-electric strength, non-conductivity, resistance to electrical breakdown
- b) mechanical strength, compression, tension, and shear
- c) useful life at operating temperatures
- d) flexibility
- e) di-electric loss

The varnishes are applied to fabrics, cotton or cambric, and baked. This process is repeated through several successive coats until a strong impervious body has been built.

In 1899 L. R. Emmett filed a patent wherein an insulating varnish was made from linseed oil and natural gums.

A modification of an insulating varnish, impregnating type, described in "Protective and Decorative Coatings" by Mattiello, Vol. III, page 231, follows:

10 gallons tung oil
20 gallons linseed oil
10 gallons falkidine
70 pounds cumar resin
30 pounds modified phenolic
3 pounds manganese drier, 6% metal
6 pounds lead drier, 16% metal
45 gallons gasoline

Heat 5 gallons linseed oil and 50 pounds of cumar resin to 600°F. and hold for one-half hour. Then add tung oil and heat to 560°F., drop temperature to 450°F., and hold two hours. Add 20 pounds of cumar and 30 pounds of modified phenolic resin and reheat to 470°F. Hold for two hours, then add 15 gallons of bodied linseed oil and 10 gallons of bodied Falkidine; reheat to 500°F. and hold one hour at 460°F. Cool, thin, and add driers.

Of necessity, it is apparent from this paper that each subject might have been treated at much greater length and in more detail. While the oils used in these subjects might be miscellaneous to the drying and semi-drying oil industry, the miscellaneous use itself is a very important factor for the specified industrial use.

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REFERENCES

1. "Palm Trees by Proxy," by J. E. Payne, Steelways, March, 1950.
2. "Fatty Acids," by Markley, 1947, pp. 425-427.
3. Kastens and Peddicord, Industrial and Engineering Chemistry, 41, 3, 438-446.
4. Kenyon, Stingley, and Young, Industrial and Engineering Chemistry, 42, 2, 202-213.
5. Mattiello, "Protective and Decorative Coatings," 1, 78.

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