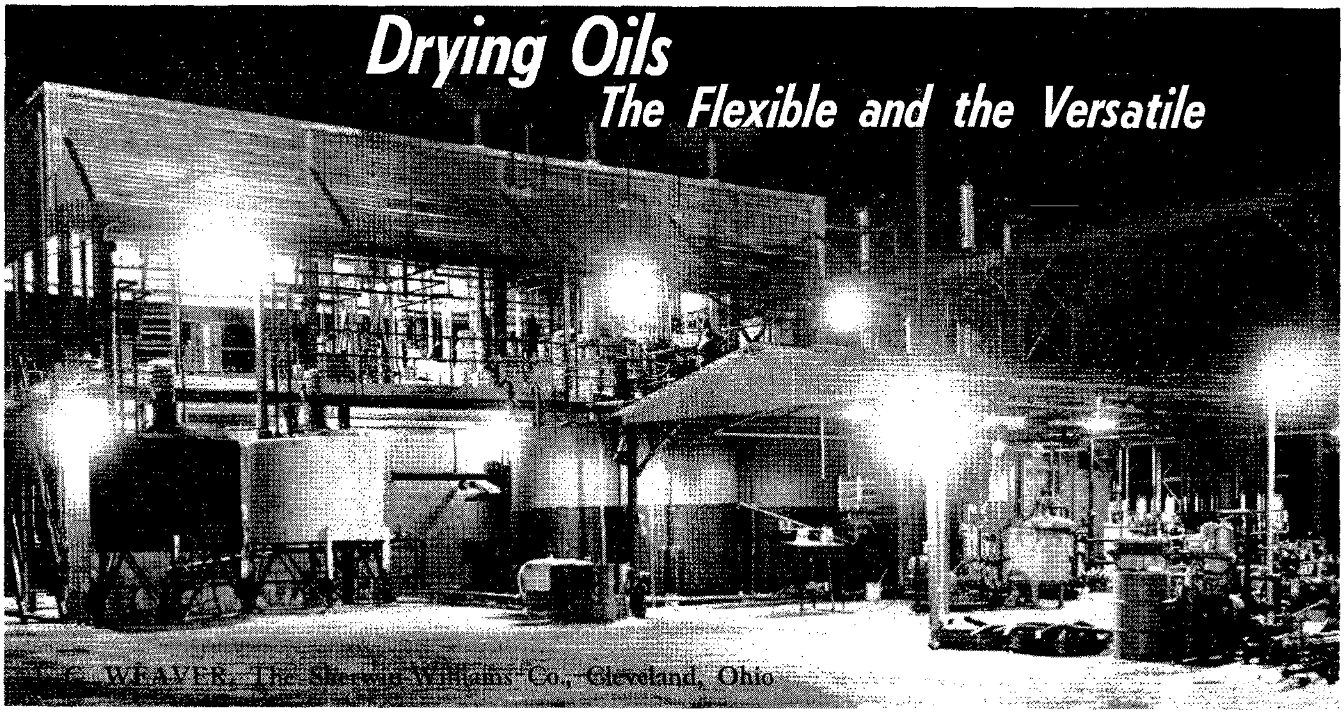

Drying Oils
The Flexible and the Versatile

[illegible] C. WEAVER, The Sherwin-Williams Co., Cleveland, Ohio

FLEXIBILITY is the keyword to the use of drying oils in paint. They help protective and decorative coatings to withstand the extremes of heat and cold and of dry and wet conditions, and the resulting dimensional changes in various substrates, particularly wood. The paint industry has grown to an annual production of more than 600 million gal with a wholesale value of over $1.8 billion. But with increases in population and in the *per capita* consumption of paint, the use of drying oils in paint has not kept pace.

Flexibility alone is not enough, and other polymeric materials are displacing drying oils in some type paints of very high performance requirements. In spite of this, more drying oils were used in paints in the last five years with an average of 470 million lb, than in the 1938 through 1942 period of five years, when the average was 414 million lb.

Versatility of commercial choice of nearly a dozen oils important to the paint industry is shown in Table I, abstracted from Bureau of Census reports for 1938 through 1962. The oils range from conjugated, "hard-drying" tung, through non-conjugated, "soft-drying" soya to non-drying coconut. Even with necessary limitations of reporting, it is obvious that linseed oil continues to be the "back bone" of the paint industry. Other important changes included the disappearance of perilla when Japan conquered Manchuria, and the mid-1940 surge in use of dehydrated castor when World War II stopped the flow of tung oil from China, causing new chemical technology to build upon expanded supplies of raw castor oil from a then vigorous economy in Brazil. Tall oil (and tall oil fatty acids) have improved wonderfully in quantity and quality as the giant paper industry diverted black liquor from pollution of streams, and separated a valuable by-product therefrom for an improved profit margin.

Versatility at a less obvious level can be read into and between the lines of Table I by chemists who have toiled in the industry over its span of years. They revised paint formulations again and again to compensate for surges and trends in prices and supplies brought on by the depression of 1938 and the post war boom of 1947, by military needs in World War II, by freezing weather in the tung groves of Mississippi, by wet weather in the Red River Valley, or by oil seed price support policies in Washington. The growing importance of safflower oil in paint as well as to polyunsaturate fat advocates is too recent to be reported separately for paint by the Bureau of Census. The Bureau of Census, Summary for 1962, reports that the 1962 crop of safflower oil totals 116.5 million lb., while the Economic Research Service, U.S.D.A., indicates the October, 1962 through January, 1963 use of safflower oil in drying oils as 15.2 million lb. It will take even longer to gauge the importance of dimorphotheca and other new oils under very active study by the regional laboratories of the U.S.D.A.

Linseed oil was used for centuries, with pigmentation by various earth colors, and hardened by cooking in, and mixing in, oxides of lead and manganese, and by treatment with heat and air in crude trade secret fashion. Fossil resins such as amber, Kauri and Congo "gums" were used for a long period, and to a small extent up to the present, to harden linseed oil in a paint or varnish film. Non-fossil natural resins, such as rosin from the exudations of U.S. Southern Pine, and related resins from several species of trees in the East Indies, served to build up and extend the technology of oleoresinous varnishes based on linseed oil. Chemical improvement of the rosin by esterification, or by incorporation of phenolic condensate or maleic anhydride, extended the use of the "hard resin" modifier of linseed oil through World War II, but their use is now declining more rapidly than the oils.

In general use, the glyceride drying oils remain the most versatile of all paint vehicles. In spite of a wide array of petrochemical monomers from which many marvelous polymers are built, no single class of synthetic polymers has displaced the glyceride oils from a substantial section of the paint economy. Over the past thirty or more years most of the petroleum refiners accumulated dark, viscous residues which they offered as drying oils to paint makers. These odorous liquids were heterogeneous mixtures of unsaturated olefins, etc., which did indeed dry to a solid film, but if they dried in hours and days at a speed comparable to linseed oil, they kept right on drying in days and weeks to a brittle film that may have shattered off of its substrate. In the last 20 years, the economical production from petroleum of ethylene, propylene, butadiene, of the vinyl families such as styrene and its homologues, the acrylates and others, have made possible some tailor-made polymers conferring outstanding qualities to paints and plastics for specialized purposes. Yet, no one class of these has yet matched the versatility of the glyceride oils.

Oil Refining and Color

Preoccupation with refining methods has become largely historical since nearly all of the commercial oils meet high standards of clarity and uniformity. A single, notable exception is that raw linseed oil, with its highly variable "foots" content, may now be one of the most non-uniform, high volume components in paints. Linseed oil suffers from its unique content of waxes and diverse phosphatides which are difficult to remove, especially with no coincident standards for edible use, outside of eastern Europe. One or all of the operations of wet degumming, alkali refining, clay bleaching, refrigeration, and filtration probably account for the refining of practically all of the oils used in paints.

Color is the one aspect of oil refining which may yet deserve major improvement in order that oils may compete successfully against acrylates and other colorless, tailor-made film formers. It is a moot question whether the high costs of sophisticated identification and exhaustive removal of color bodies from whole oils and fatty acids could extend profitably their competitive reach in white and pastel enamels. Perhaps this sophisticated identification should span in detail both the color compounds in the oil and the colors that develop in the film at various stages of its life. Since after-yellowing is one of the principal reasons for encroachment by acrylates and other synthetic monomers, this problem should not be ignored.

From Limpid Oil to Dry Paint

Converting a limpid oil to a solid, flexible, and useful film remains the central objective of drying oil technology. The classic methods of polymerization by head, with and without catalysts or oxygen, remain important for linseed and the more important oils. Most of this is performed in closed reactors of 1,000 gal or larger size in the absence of air and often under partial vacuum to keep acid value to a low level. With a growing preference for white and light shades of paint there is less opportunity for the dark, viscous oils produced by air blowing.

Viscosities of linseed and other oils used in house paints prior to World War II were relatively low, generally without much volatile solvent, and in the two to five poise viscosity range needed for brush application. War time conservation measures required higher viscosity oil in more volatile solvent, with consequent faster initial drying and less penetration of a porous substrate such as wood or old paint. This formulation showed better uniformity on the surface, and greater exterior durability through a more constant pigment-to-binder ratio and controlled penetration, and is still used at present.

Competition in recent years by latex made from acrylate esters, vinyl acetate, and other monomers has brought new *high standards in drying speeds, tint retention, and non-yellowing.* With this challenge to a long established use of oil came the realization that a still higher degree of polymerization of oil, plus dispersibility in water, could yield an oil-based paint of fast drying speed, and better penetration of porous substrate or old paint than could be achieved with unmodified latex. The higher degree of polymerization left fewer reactive sites in the oil molecule for slow reaction and degradation in the paint film and consequently exhibited better tint retention and slower chalking. The Northern Regional Laboratory, U.S.D.A., and several oil and paint companies are currently carrying this development into commercial realization. The prospects for it seem bright.

Alkyds are the big class of paint intermediates using the fatty oils. Some of the linseed and most of the soya, tall, coconut, raw castor and dehydrated castor oils are combined into alkyds in various ratios, and sometimes modified by rosin, styrene, and various other monomers and resins. With prices of 13¢/lb for phthalic anhydride and 18¢/lb for glycerine, the raw material cost of glyceryl phthlate is about 16¢/lb. With most of the major oils for paints priced at 10–15¢/lb, the bulk manufactured costs of most alkyds lie between 15 and 20¢/lb on a solids basis. Alkyds are likely to continue for some years as the "work horses" of the paint industry in shear volume of production and great diversity of formulation.

Alkyd modifications by reactive monomers are likely to extend their span of commercial life even further. Already, considerable styrene is used for copolymerization in oil modified alkyds, with improvement in drying speed, and with attractive economy. Styrene, at about 11¢/lb, is challenging long established rosins at 10–14¢/lb as an economic and technically superior hardener of oils for paint. The growing commercial list of polymerizable vinyl monomers such as vinyl toluene, acrylonitrile, methyl methacrylate, and relative acrylate esters all serve to extend as well as rival the position of fatty oils in paint. Even more complex combinations of these with oils are likely for the future.

Urethanes from combinations of oils and isocyanates, such as toluene diisocyanate, are enjoying new commercial success for good weather resistance and superior abrasion resistance. This facet of the paint industry is expected to grow.

Miscellaneous modifications of oils, illustrated by low temperature, air-blown soya oils for lacquers are epoxidized soya oil for stabilizing vinyl chloride polymers, are far too

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TABLE I

Fatty Oil Consumption in Paints in the U. S. Shown in Millions of Pounds Consumed per Year
Abstacted from Reports of the U. S. Dept. of Commerce, Bureau of Census

	Total	Tung	Oiticica	Castor dehydrated	Fish	Perilla	Linseed	Soya	Tall oil	Castor raw	Coconut
1938	358	78			16	24	217	15		6	.4
1939	423	82			25	29	247	22		11	.7
1940	435	53			31	15	270	30		24	1.2
1941	571	49			41	5	374	42		44	.9
1942	282	7			12	1	210	14		31	.2
1943	444	10	3	13	25	1	367	20		4	w
1944	536	8	8	64	38		385	19		13	w
1945	497	17	13	44	43		322	26		8	—
1946	530	25	15	25	36		362	30		4	.2
1947	615	69	9	28	34		349	89	9	5	.5
1948	626	92	5	38	27		314	100	22	8	.9
1949	505	80	w	26	12		222	90	18	6	w
1950	601	80	5	32	21		243	87	20	7	3.4
1951	571	54	8	19	22		320	61	27	5	3.5
1952	551	41	8	12	28		303	73	25	3	3.5
1953	556	41	7	12	23		294	81	25	4	4.7
1954	500	40	6	11	12		257	80	23	3	5.0
1955	514	40	5	w	16		277	93	29	4	7.2
1956	482	39	5	w	14		256	90	26	5	5.7
1957	466	34	5	w	11		249	84	26	6	5.9
1958	424	29	4	w	12		231	79	21	5	w
(1959:	BUREAU OF CENSUS CLASSIFICATIONS REVISED EXTENSIVELY)										
1959	476	32	w	w	w		271	99	21	20	w
1960	486	30	w	w	w		289	100	18	20	w
1961	487	28	w	w	w		298	91	18	20	3.9
1962 P	474	26			w		298		17	20	4.0

w: Withheld, not reported separately
P: Preliminary estimates

Drying Oils . . . .

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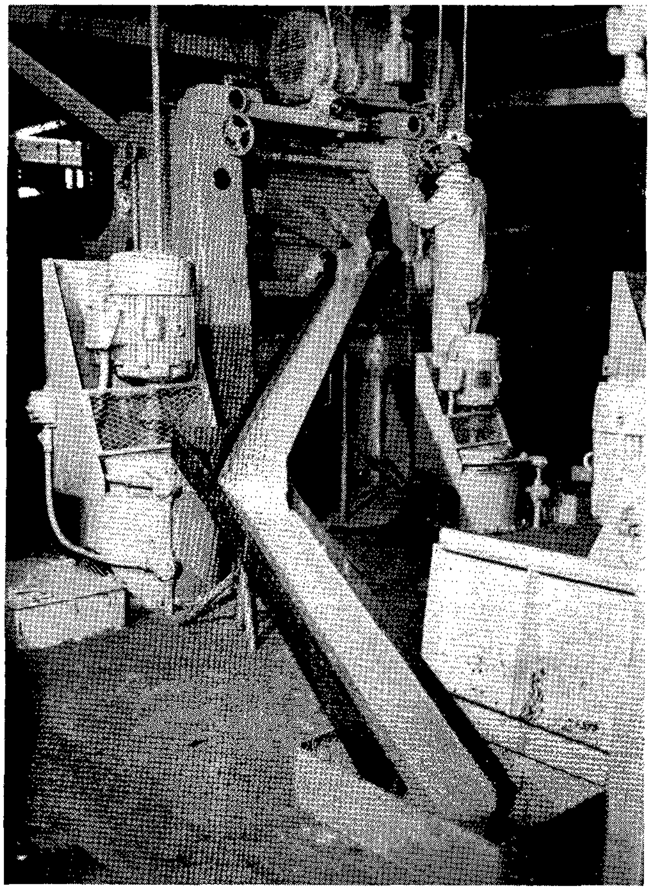
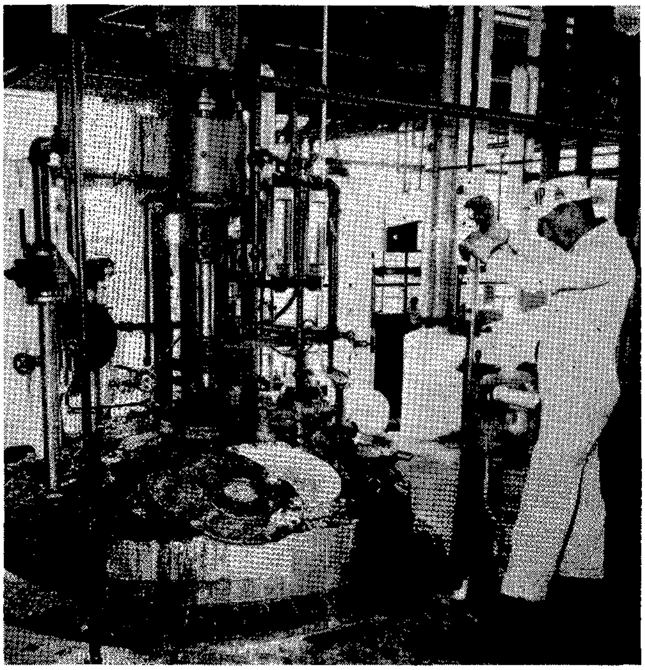
numerous for discussion, or even for listing. They serve to emphasize the great diversity of the use of oils in paints.

Shortcomings of the fatty oils need continued study if they are to maintain their place in the paint industry. Some of these have been mentioned or implied in the foregoing. Yellowing, odor, embrittlement with age, inadequate resistance to chemical attack and fungal, and microbial decay are among the more obvious inadequacies. Tensile strengths, elongations, freeze-thaw and abrasion resistances, paleness, and chemical stability are found to higher degree in some of the synthetic polymers specifically designed for one or more of these properties. They range in price from the 15–25¢/lb span of polystyrene and polyvinyl chloride to the 50¢–$5/lb span of acrylate, epoxy phenolic, or fluorocarbon polymers. It is not likely that fatty oils can be chemically tailored to meet all of these challenges, but the versatility of these oils leaves a lot of opportunity for search in that direction.

Chemically vulnerable points in the dried films of oil obviously include impurities, the ester group, residual unsaturation and potential free radical sites in the fatty acid chain, and chemical abuse in the processing of the oil and in its drying in the film. Even greater purity of the original oil, plus more sophisticated and complete polymerization or "vulcanization" of the oil prior to formulation into paint are continuing challenges. The great amount of effort on these problems reported in detail in patents and in the published technical literature over recent decades will continue. Earlier attempts at overcoming the vulnerability of the ester group by gross pyrolysis may be supplanted by more specific conversion to an inert grouping, without dark by-products. Better catalysts or co-reactants may be found to use up all of the unsaturation before and during film formation, not leaving it for rapid degradation of the film. Along with these should come improved resistance to biological attack. Improved additives or stabilizers for ultraviolet screening, as antionidants and biocides are being developed every year.



A Five-Roll Plant Mill shown operating in the general paint manufacturing area at Sherwin-Williams Co., Carland, Texas.



A closed reactor for Oils, Alkyds, Varnishes, etc.

For example, there is a great deal of current research on the problem of controlling after yellowing of linseed oil paint films. Likewise, the tendency of linseed oil paint films to blister on moist wood substrates, particularly in the presence of zinc oxide shows promise of yielding to research.

An application for linseed oil which holds forth considerable promise of success in utilizing relatively large quantities of the product is the coating of concrete surfaces to inhibit scaling due to repeated freeze-thaw cycles or to the corrosive action of the common anti-freeze agents, notably chloride salts.

A number of mid-western states, including Illinois, Iowa, and Missouri, are using the material in large quantities and its use is spreading rapidly.

In general, the paint industry has in a few decades, evolved from craftsmanship based on traditional blends of white lead and raw linseed oil to a highly technical and specialized industry producing hundreds of types of protective and decorative coatings. Some of them are proved to serve in exterior protection for 10 or even 20 or more years. Some of these high performance paints are based in part on fatty oils and continued technical advances can be confidently expected to maintain a position for these oils in the paint industry.

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• *New Members*

Active

Richard H. Christensen, Quality Control Manager, General Foods Corp., Chicago, Ill.

Donald W. Codding, Junior Scientist, Univ. of Minnesota, Hormel Institute, Austin, Minn.

Roger A. Eisenhauer, Chemical Engineer, Northern Regional Lab., U.S.D.A., Peoria, Ill.

Juan B. Fenjves, Manager, Proquim C.A., Caracas, Venezuela, S.A.

William F. Goldsmith, Project Controller, R & D, Union Carbide Chemicals Co., South Charleston, West Va.

Lloyd A. Hall, Vice President, R & D, Pilot Chemical Co., Santa Fe Springs, Calif.

Ira Katz, Research Associate, University of Maryland, Dept. of Dairy Science, College Park, Md.

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