cottonseed oil 45%, and "other vegetable oil," mostly coconut oil, 10%. Future trends in this market depend not only on quality improvement and promotion effort but on further legislative recognition of mellorine's rightful place in the market as a wholesome, nutritious food-product.

The remaining consumption of vegetable oils in foods, shown in Figure 12, is classified as "other edible products." This group includes consumption in bakeries, prepared flours, canned soups, candy, and so on. Figures are not available for individual products in this group.

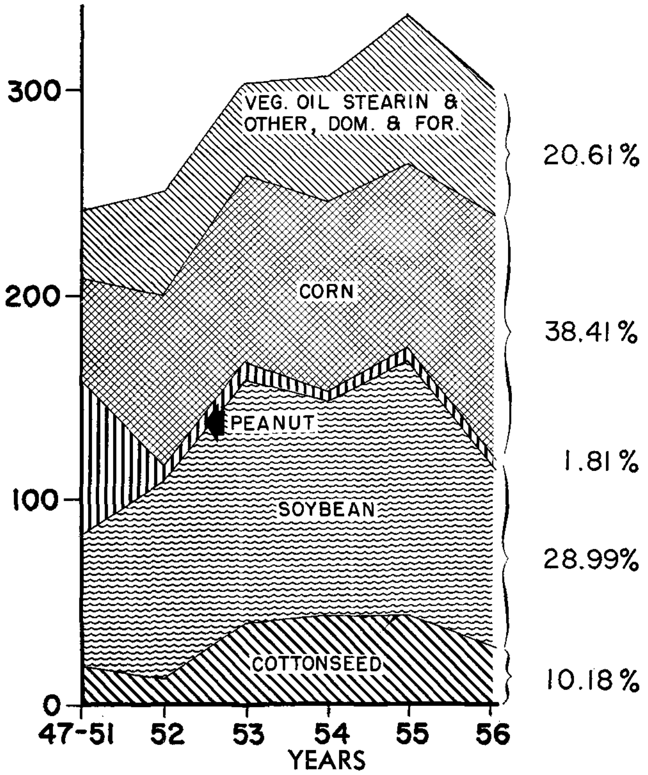

Fig. 12. Estimated U. S. factory consumption of vegetable oils in the production of other edible products (million pounds).

The total consumption of vegetable oil in "other edible products" amounted to 304 million pounds last year. As is apparent in the chart, the total consumption rose from 251 million pounds in 1952 to a high of 339 million pounds in 1955, then declined to 304 million pounds in 1956. This decline reflects again increased competition from lard and edible tallow, as occurred in shortening in the same two years. Corn oil, for the first time, is the principal oil used, accounting for 38% or 117 million pounds in 1956. Soybean oil, at 29%, was the second largest supplier while cottonseed accounted for 10%.

Inedible products represent only a fourth of vegetable oil consumption, in such products as paints and varnishes, soaps, printing inks, linoleum, oil cloth, lubricants, and greases. Linseed is the principal oil consumed in inedible products, along with domestic and foreign oils other than those represented as principal factors in the edible products field. Since cottonseed oil is a relatively small factor in inedible products, only a few brief comments will be offered. Coconut oil is about the only vegetable oil now used in the soap market. The largest natural competitor is and has been inedible tallow and grease. Consumption of vegetable oils in soap in 1956 was almost exactly half the average of the 1947–51 period. Use of tallow and grease is off however by more than 40%. Increased use of synthetic detergents is the obvious explanation; these now account for two-thirds of the total consumption of soaps and detergents.

In paints and varnishes, and for that matter in all uses of drying oils, no significant shift is observable in the total use of fats and oils. The most interesting factor in paints and varnishes is a shift away from linseed oil toward soybean oil. Paint formula changes, utilizing more alkyd resins, which adapt semi-drying oils to drying oil uses, are responsible for this shift.

Total production of vegetable fats and oils has increased steadily from 1951, with the increase in cottonseed and soybean together on the order of about 40%. Domestic use, like production, has also increased for these commodities, but it has not increased to anything like the same extent. For cottonseed and soybean together the increase amounted to only 10%. Although domestic stocks increased slightly, the amount of additional oil in the stocks is negligible as compared with either production or use. The only reason that there has not been a disastrous accumulation of food fats and oils has been the sharp increase in exports resulting principally from government programs. Exports of cottonseed and soybean oils together, for example, more than tripled in the period from 1951 to 1955. The outlook for 1957 is for continuing exports of these two oils at about the same level as last year, approximately two billion pounds.

Acknowledgment

The authors are grateful to Robert V. Miraldi for preparation of the charts used in this paper.

Note: The statistics on which this paper is based are published annually under the same title by the National Cotton Council. Copies may be obtained without charge, on request.

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Drying Oils

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This paper will discuss some economic factors which suggest the present large value of drying oils as chemical intermediates. Then it will consider two chemical reactions of current importance in making more useful industrial products out of fats and oils.

In any historical approach to drying oils (2) it is easy to overstress the early importance of such drying oils as linseed oil to the paint industry and relatively easy to neglect the current substantial position of these oils in industry in modern times. Drying oils are now complemented by an ever-increasing number of synthetic raw materials which attract the attention of chemists. But chemists cannot afford to overlook what's new in drying oil chemistry. A substantially larger research effort is now being devoted to the chemistry of drying oils than in any period previously. This work is yielding more and more information about the basic nature of drying oils, the effects of environment on their behavior, and ways to modify them to bring out their most favorable properties. The natural adaptability of drying oils for service in paints in combination with their low cost makes them especially rewarding targets for paint research. They also warrant attention for wider industrial applications.

Economics

For a company's purchasing agent, the decision to buy, or not to buy, drying oils on a particular day will be dependent upon minor fluctuations in price which may cover only a fraction of a cent per pound. It is not beneficial for research and development people to be concerned about minor fluctuations in the commodity market. It is important however for them to be aware of the general level and the trends in prices. Also it is important for them to look at price and property relationships.

Drying Oil Prices. Historically, individual drying oils have been subject to rather wide fluctuations in price. Shortages because of war, drought, or speculative interests often in the past have resulted in rapid and substantial price changes in drying oils. For example, raw linseed oil rose from a 1945–46 average price of 14.3¢ per pound to 29.9¢ per pound in 1946–47. At about the same time crude menhaden oil jumped freom 11.1¢ a pound to 18.6¢ a pound, average price.

Such major price changes may have had appeal for speculators, but they were discouraging to business men who needed a more stable price on raw materials for satisfactory operations. Hence it is of significant importance to industry that technological progress seems to have helped in smoothing out the price spreads among drying oils. Also it is of major importance that the current prices of these raw materials have been running below the levels of 10 years ago, at a time when most materials have risen significantly in cost.

There is now a world surplus of fats and oils, which appears likely to be with us for some time. At least there is an economic surplus, whatever may be the oil needs of impoverished nations.

L. A. Goldblatt has pointed out (4) that interconvertibility is narrowing the price spreads among the various oils. Individual oils which become scarce because of limited supply no longer are likely to jump wildly out of price line. Alternative oils from stocks in surplus can be effectively substituted. For example, randomization methods have enabled lower cost lard to compete more satisfactorily with vegetable oils in shortenings. This has narrowed the price differential in the edible oils group rather dramatically.

In the case of drying oils the preference for an individual oil on the basis of properties especially desired in a particular service dominates the choice. However chemistry increasingly is showing us how to achieve similar properties from different drying-oil base stocks. Chemical technology promises to make the various drying oils more nearly equivalent, and this certainly will tend to narrow their price spreads. The increasing competitive pressure from petrochemicals is likely to have a stabilizing effect on the price level of the drying-oil group.

The data in Table I demonstrate our thesis only in part since the spread at year's end of 1956 was somewhat greater than at the close of 1954. But at the time of writing, April 22, 1957, the comparable figures show a slightly smaller spread of 11.5 to 25.6¢ a pound.

TABLE I
Comparison of Drying Oil Price Ranges
(Cents per pound)

	December 1952	December 1954	December 1956[b]
Dehydrated castor oil, tanks (New York)	31.1	21.6	26.1
Linseed, raw, tanks (Minneapolis)	14.8	12.6	13.4
Menhaden, light-pressed, tanks (New York)	11.1	11.0	11.5
Oiticica, drums (New York)	25.4[a]	16.5	17.5
Soy, crude, tanks (Decatur)	12.9	12.5	14.0
Tung, drums, C. L. (New York)	36.2	22.2	25.0
Range	11.1–36.2	11.0–22.2	11.5–26.1

[a] Year average. [b] Prices December 31, 1956.

Cost forecasts always must reckon with some "imponderables." In the case of drying oils politics must be considered in any price projections, and this certainly increases the chances for error in the estimate. Government support for the prices of particular farm crops is likely always to affect the prices for individual oils in some measure. The government's PL 480 program will directly affect the price of drying oils which are also edible, such as soybean oil. However the price moves of individual oils within the group promise to be smaller than in times past, and movement of the group price-level now appears to have been minimized.

In Figure 1 is shown graphically the recent price history of linseed oil. There has been relatively little change in the past five years. For some months now the price of raw linseed oil has been stabilized near 13¢ a pound (Minneapolis). At present prices linseed oil will compete as a chemical raw material with

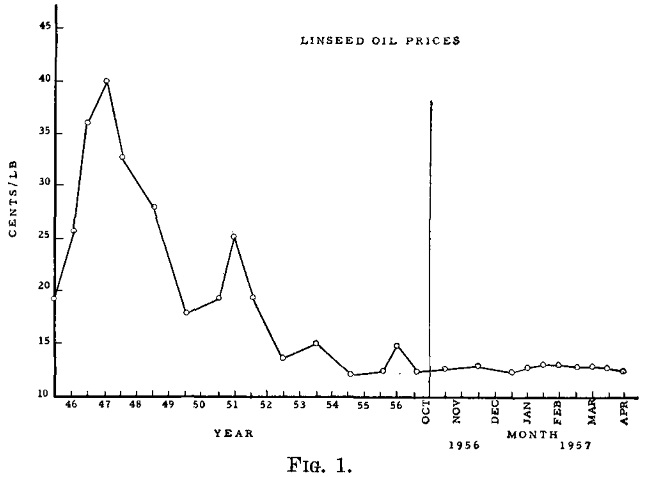


FIG. 1.

the following chemicals (delivered prices in parentheses): vinyl acetate (16.5¢ a pound), styrene (16¢), butadiene (15–16¢), methyl methacrylate (30¢), and other chemicals of interest to the coatings and plastics industry. As such, linseed oil warrants renewed attention from industrial chemists who are looking for versatile, low-cost raw materials. In particular, linseed oil has a recognized natural talent for service in exterior house paints. Therefore we can propose it as an attractive chemical building block for the future's improved exterior house paints whether water-based or applied from solvents.

Businesses which employ drying oils as raw materials and as chemical intermediates will benefit from the greater price stability which now seems in prospect on the basis of recent market experience.

Consumption of Drying Oils. As relatively low-cost raw materials which can be converted to direct use in vehicles with little processing, or readily modified for special uses, the various drying oils have been consumed in large quantities by industry.

In Table II the running record of consumption is high-lighted for the United States in the following products: paints, varnishes, floor coverings, printing inks, core oils, synthetic resins, insulation, linings, packings, coated fabrics (including oil cloth), and caulking compounds. The fraction used in coatings has fluctuated between 75–85% in the period reported.

TABLE II

Drying Oil Consumption in U.S.A.[a]—Civilian Products

Year	Total	Per capita
	(million lbs.)	*(lbs.)*
1934	601	4.7
1939	822	6.2
1944	845	6.5
1949	911	6.1
1954	882	5.5
1955	1,031[b]	6.4[b]
1956	1,049[b]	6.3[b]

[a] Source: U.S.D.A.'s Fats and Oils Situation No. 184, p. 20.

[b] Preliminary.

In Table III there is a breakdown of drying oil consumption in total by kinds of oils. It is of special interest that the drying oils consumed in the largest quantity are now all domestic in origin. Linseed oil has been relatively constant in the quantity consumed annually over the twenty-year period. Its relative share of the market has declined however from about 75% to less than 45%. Soybean oil has been the largest gainer, now at nearly 25% of the total. Tall oil now accounts for more than 10% of the consumption. The consumption of fractionated tall oil fatty acids in drying oil service appears to be rising as these products have become more widely available.

In the miscellaneous group oiticica is one of the larger single entities, with imports running about 10,000,000 lbs. a year—about 1% of total drying oils consumed. Safflower is a domestic drying oil which seems to be growing in importance. Sunflower oil is a minor factor now but may well become more important.

Modified Drying Oils

Various routes are available for modifying drying oils simply to enhance particular properties or to arrive at something quite different in all respects from the starting materials. Ozonolysis of oleic acid to produce new chemical intermediates has become commercially important, for example. Very widely used are addition reactions, such as the addition of maleic anhydride or cyclopentadiene to drying oils. Copolymerizations with vinyl compounds involving reaction of double bonds and interesterifications involving a change at the ester linkage are especially important.

In the past quarter century oil-modified alkyd resins prepared by the alcoholysis of oils and supplementary re-esterification with dibasic acids have commercially become the most important chemical modification of the oils. The paint industry currently consumes more than a quarter-billion pounds per year of such products.

This paper will consider only two of the newer ways to modify oils which promise to increase in commercial importance: reactions with vinyl toluene and with diisocyanates. In some degree the products made in this fashion will compete with other oil-based products. These products also promise to enter types of service for which oil-based products previously were unsatisfactory. In our opinion these reactions are among the most attractive now available for extending the industrial consumption of drying oil-based products. Although most of the data now reported are tied to use in coatings, it appears that these same reactions also will be useful in making oil-based placticizers, plastics, textile modifiers, paper additives, and other industrial products.

Vinyl Toluene-Modified Oils. Various substances containing the readily polymerizable vinyl group, $\mathrm{CH_2{=}CH}$—, will react with drying oils at elevated temperatures, especially in the presence of organic peroxide ("free radical") catalysts. Styrene (vinyl benzene), alpha-methyl styrene, and vinyl toluene have had the largest commercial significance by happy virtue of the favorable coating properties which they confer and their relatively low cost (1). Divinyl benzene also finds use in some copolymerization recipes to increase the molecular weight of the products through cross-linking.

Until recently commercial interest in this country largely centered on the "styrenation" of oil-modified alkyd resins rather than the styrenation of the drying oils themselves. A large amount of research effort has been aimed at improving the properties of the sty-

TABLE III

U. S. Consumption of Various Oils in Drying Oil Products[a]—Total
(By millions of pounds)

Year	Linseed	Soy	Tung	Fish	Castor	Tall	Misc.	Total
1930–34 (Avg.)	433	12	97	22	2	......	19	585
1935–39 (Avg.)	514	22	118	39	7	......	74	774
1944	688	37	10	47	90	7	38	917
1949	428	220	103	26	51	53	93	974
1954	498	209	48	23	38	117	84	1,017
1955	504	274	50	33	63	123	125	1,172
1956	519	300	50	26	73	146	102	1,216

[a] Source: U.S.D.A.'s Fats and Oils Situation No. 177, p. 28, and No. 183, p. 33.

renated oils (6, 7), and separate products tailored to meet a wide range of services are now available. Vinyl toluene has certain advantages over vinyl benzene (styrene) in such reactions, especially in better compatibility properties. The Dow Chemical Company has been responsible in major fashion for pioneering and promoting the modification of drying oils with vinyl toluene. Their coatings technical service department now provides instruction sheets which suggest recipes for the manufacture of vinyl toluene/oil flat paints, industrial enamels, masonry sealers, and other related products. Such materials may contain 20–70% vinyl toluene. A wide variety of drying oils can be used acceptably.

Vinyl toluene and oil may be copolymerized either by the solvent method or at "100% solids" in a solvent-free system. The solvent method has been generally favored because of the better control which it affords; less vinyl toluene homopolymer is formed in solution. But the reaction proceeds more slowly in solvents than in bulk, and the solvents may not be desired in the product. If solvent-free products are desired, the incorporation of some alpha-methyl styrene in the vinyl toluene tends to improve the homogeneity of the bulk reaction, apparently because of the lower reactivity of alpha-methyl styrene and its stopping effect on growing vinyl toluene molecules.

Current theories of vinyl polymerization hold that the formation of an active free radical, for example, by thermal decomposition of a free radical catalyst is necessary to initiate the polymerization. Propagation then proceeds by a chain reaction involving the addition of vinyl monomer units. This chain reaction is then terminated when the growing polymer runs low on the energy which is needed to activate more monomer molecules, by steric hindrance, by striking an inhibitor molecule, or by contact with another free radical.

In practice, ditertiary butyl peroxide is the commonly used free radical catalyst. Unsaturated bonds on the fatty acid radicals of the oils appear to be the chief terminators for the growing vinyl toluene chains. In cases where oxidized oils are being treated, it appears that the thermally decomposing hydroperoxides of the oil may act as polymerization initiators as well as chain terminators.

As representative of current commercial vinyl toluene/oil products Keltrol 1001 (in mineral spirits), Keltrol 1013 (in xylene), and Keltrol 1074 (in VM&P naphtha) are cited. These are low-cost, quick-drying enamel vehicles with typical analyses and properties, as shown in Table IV. Keltrol 1074 is significantly lighter in color than the other products but is essentially similar in other respects. An equivalent "plastic" form of these Keltrol resins at 100% solids is under experimental development. Such solid products in finely divided form will become insoluble in contact with air, evidently as a result of oxidative reaction. There is no real problem however in keeping the resin in suitable form for use.

TABLE IV

Analysis and Drying Properties of Vinyl Toluene/Oil Copolymers

	Keltrol[a] 1001	*Keltrol*[a] 1013	*Keltrol*[a] 1074
Solvent	Mineral spirits	Xylene	VM&P naphtha
Viscosity (Gardner at 25°C.)	Y ± 1 (bubble)	Z±1 (bubble)	Y—Z
Color (Gardner)	7 (max.)	7 (max.)	5 (max.)
Acid value	5 (max.)	5 (max.)	5 (max.)
% Solids	60 ± 1%	60 ± 1%	60 ± 1%
Weight per gallon	7.6 lbs.	7.9 lbs.	7.6 lbs.
Tack-free dry	30 min.	15 min.	15 min.
Sward hardness (24-hr.)	29	26	28

[a] Registered trade mark, Spencer Kellogg and Sons Inc.

Another recently developed vinyl toluene-modified oil of longer oil length is identified as XP-1059. This is a low-cost, architectural flat vehicle with versatile properties, which are summarized in Table V. The low after-odor of paints based on this product during the air-oxidation phase of drying is attractive; there is significantly less acrid after-odor than is characteristic of alkyds. Excellent working properties enable the paint formulator to prepare from this single vehicle a full range of satisfactory paints from top quality to inexpensive, highly pigmented products. The vehicle is somewhat thixotropic, and paints based on this vehicle have sufficient "false body" to minimize pigment settling.

TABLE V

Typical Analyses and Properties of XP-1059,[a] a Vinyl Toluene/Oil Copolymer

Solvent	Odorless mineral spirits
Nonvolatiles	40% ± 1
Viscosity	Soft thixotropic gel
Color (Gardner)	6
Acid value	1.7
Weight per gallon	7.0 lb.
Specific gravity	0.842
Dry	Paints dry tack-free in 1–2 hrs. but have good wet edge retention
Pigmentation	Wide PVC range (55–75) with good color uniformity and no hard settling of pigment in storage
Washability	Good scrub and alkali resistance

[a] XP-1059 is an architectural, flat vehicle now available from Spencer Kellogg and Sons Inc. as Keltrol 1059.

Diisocyanate-Modified Oils. During World War II the so-called urethane oils were developed in Germany. It is of considerable interest that these products, which were promptly picked up by the first U. S. teams to enter Germany after the war, did not find early commercial acceptance here. No doubt the high prices of the diisocyanate components at the time were dampening to initial enthusiasm. More recently, as aromatic diisocyanates have been manufactured here in increasing quantities for use with polyesters in the production of foams (3), urethane oils have become the center of a revived interest. Papers presented in a two-day symposium before the Paint, Plastics, and Printing Ink Division of the American Chemical Society in Atlantic City in the Fall of 1956 demonstrated substantial new research activity. Currently the urethanes appear on the verge of fulfilling their promise to satisfy certain critical needs in the coatings industry (5, 8).

The isocyanates are extremely reactive substances, which combine readily with any material containing an active hydrogen. In the reaction with water, for example, carbamic acids are produced, which decompose to yield amines and carbon dioxide:

$$RNCO + HOH \longrightarrow RNHCOOH \longrightarrow RNH_2 + CO_2$$

Since the amines also contain active hydrogen, they react with additional isocyanate to yield substituted ureas:

$$RNCO + RNH_2 \longrightarrow RNH\overset{\overset{\displaystyle O}{\|}}{C}NHR$$

The reaction with water is an important step in the manufacture of polyurethane foams. For most other applications of isocyanates the reaction with water tends to be a trouble-maker, necessitating anhydrous conditions in handling the reagent. The reaction with

TABLE VI

Comparison of Urethane Oils with Common Paint-Vehicles (Air-Dry)

Vehicle nomenclature	Nature		Est. relative cost[c]	Pot-life	Dry time (hrs.)			Sward hardness		Weatherometer data Clear finishes on wood	
	Package	Type			Set	TF	Hard	1 day	1 week		
(A) XP-1077	1 can	Urethane drying oil (Co. catalyst)	4	Inf.	¼	1½	3½	5	20	Little effect	500 hrs.
(B) XP 1066/TDI	2 cans	Modified castor/TDI[a] (Co. catalyst)	5	8 hrs.	¼	6	9	5	25	No effect	500 hrs.
(C) XP-1093/1087	2 cans	Modified oil/TDI/Amine catalyst	2	2 wks.	¾	7	9	8	20	Some cracking	500 hrs.
(D) 278V274	2 cans	Modified oil/TDI	1	16 hrs.	¼	5	7	35	70	Loss of gloss	400 hrs.
Polester/DI	2 cans	Commercial Polyester (TDI-TME[b] floor varnish)	1	3 days	¼	2	10	30	65	Some cracks	500 hrs.
Epoxy resin	2 cans	Amine catalyzed hard epoxy resin (4% ethylene diamine)	5	8 hrs.	½	1½	6	15	30	Peeling	350 hrs.
Epoxy ester	—	Commercial high quality epoxy ester	3	Inf.	¼	1¼	24	2	15	Little effect	500 hrs.
Chlorinated rubber	—	20 cps. chlorinated rubber	5	Inf.	¼	½	4	15	25	Failure	150 hrs.
Styrene/butadiene	—	Commercial synthetic rubber vehicle	6	Inf.	¼	1½	4	5	15	Failure	150 hrs.
Alkyd (med. oil)	—	Commercial medium oil alkyd	8	Inf.	½	2½	23	2	10	Damage to wood under film	500 hrs.
Tung/phenolic	—	Commercial spar varnish	7	Inf.	2	6	21	2	15	Failure	350 hrs.

[a] TDI: Toluene diisocyanate (blend of 2,4 and 2,6 isomers, 80/20). [b] TME: Trimethylol ethane. [c] Relative cost of vehicles on comparable basis to user, 1 = highest cost. (A–D): Experimental urethane vehicles (Spencer Kellogg and Sons Inc.).

water vapor also plays a helpful part however in the curing of certain coatings and adhesives.

In large measure the new industrial uses of isocyanates involve the reaction with alcohols to form urethanes:

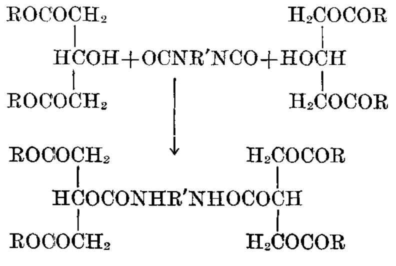
$$RNCO + R'OH \longrightarrow RNHCOOR'$$

When this reaction is carried out between diisocyanates and glycols, linear polymers result:

$$nOCNRNCO + nHOR'OH \longrightarrow OCNRNHCOOR'O\text{-}(CONHRNHCOOR'O)_nH$$

Alcohols containing three or more hydroxyl groups on reaction with diisocyanates will form cross-linked, network polymers.

As originally developed in Germany, drying oils were alcoholized with polyhydric alcohols and then reacted with a diisocyanate. For example, linseed oil was treated with glycerine to form a diglyceride, which then was reacted with diisocyanate:



$$\begin{array}{c} ROCOCH_2 \qquad\qquad H_2COCOR \\ HCOH + OCNR'NCO + HOCH \\ ROCOCH_2 \qquad\qquad H_2COCOR \\ \downarrow \\ ROCOCH_2 \qquad\qquad H_2COCOR \\ HCOCONHR'NHOCOCH \\ ROCOCH_2 \qquad\qquad H_2COCOR \end{array}$$

Such an oil, catalyzed with metallic driers, will air-dry rapidly to yield films with greatly enhanced physical properties.

In these reactions it is not customary to prepare a pure diglyceride; rather the normal alcoholysis mixture is used with some monoglyceride and triglyceride also present. The monoglyceride, having two hydroxyl groups, will form linear polymers on reaction with the diisocyanate. If the alcoholysis is carried out to yield a monoglyceride composition (rather than diglyceride), then higher polymers will predominate when the mixture is treated with a chemical equivalent of the diisocyanate.

By varying the proportions of polyhydric alcohol and drying oil, it is thus possible to produce final urethane oils that have a considerable range in film properties.

In place of an alcoholized drying oil, castor oil can be used to advantage in reaction with diisocyanates. In this case the 12-hydroxy group of ricinoleic acid, which constitutes 85% of the fatty acids in castor oil, provides the points of reaction with diisocyanates.

The National Aniline Division of the Allied Chemical and Dye Company has been especially active in promoting interest in such systems (9). Their recipes normally allow for a stoichiometric excess in diisocyanate (one mol of trifunctional castor oil with three mols of bifunctional diisocyanate) and include a solvent and a tertiary amine catalyst. N-methyl diethanol amine is especially recommended as a "reactive catalyst." Speed of dry in films can be controlled by the amount of catalyst added. In general, compositions with the fastest dry will have the shortest pot-life.

For making urethane oils, the mixed isomers of tolylene diisocyanate at present offer the best combination of price and properties. (Nacconate 80 of Allied Chemical is made up of 80 parts of the 2,4 isomer and 20 parts of 2,6.) The 2,4 isomer is the more reactive and, when used at 100%, results in urethane oils containing a minimum of free diisocyanate. Diphenyl methane 4,4′-diisocyanate has the advantage of lower volatility and yields urethane oils with some points of superiority, but currently it is substantially higher in price.

As for the oils which are used in these reactions, the possibilities are relatively unlimited. Of particular interest at present are special low moisture grades of castor oil, which carry less than 0.05% of water, and castor oils modified to have an increased hydroxyl value. (Spencer Kellogg's XP-1066, for example, has a hydroxyl number of 275 whereas normal castor oil has a hydroxyl value of 163.) Actually the moisture level of the castor oil is not critical, but it should desirably be low. For reproducibility in performance a reasonably constant moisture content is required in the system.

As for the properties of urethane oils, these will vary considerably, depending upon the extent of modification with diisocyanate. In general, as compared with normal drying oils, the urethane oils will yield coatings with greater hardness, higher gloss, good abrasion-resistance, improved water-resistance, better resistance to acids, alkalies, and solvents, and greater film strength. These improvements are gained at some sacrifice in color since the urethanes as a group tend to yellow, especially those containing a high proportion of isocyanate. Some of these materials with the greatest chemical resistance are difficult to pigment and usually require two-can systems for satisfactory shelf-life.

TABLE VII

Comparison of Chemical Resistances of Air-Dried (7-Day) Films from Urethanes and Reference Vehicles

	Water			Mineral spirits			Xylene			½% Tide solution			½% Acetic acid			30% HCl			25% NaOH		
Vehicle	*SS*	*D*	*F*	*SS*	*D*	*F*	*SS*	*D*	*F*	*SS*	*D*	*F*	*SS*	*D*	*F*	*SS*	*D*	*F*	*SS*	*D*	*F*
XP-1077	50	U	95	95	U	U	U	U	4	70	U	U	70	U	U	50	4	70	<4	O	<24
XP-1066/TDI	70	U	U	50	U	U	U	U	<4	120	U	U	70	U	U	U	50	U	U	U	U
XP-1093/1087	50	U	U	O	U	25	U	U	<4	70	U	U	50	U	U	25	25	70	70	U	U
278 V 274	U	U	U	U	U	U	O	U	U	U	U	U	U	U	U	U	145	U	U	U	U
Polyester/DI	U	U	U	U	U	U	U	U	U	U	U	U	U	U	U	U	U	<4	145	U	U
Epoxy resin	25	25	U	120	U	U	95	U	U	O	—	<4	—	—	< ¼	50	U	U	70	U	U
Epoxy ester	25	U	70	70	U	U	—	—	< ¼	70	70	95	50	O	120	70	50	U	25	95	U
Chlorinated rubber	U	U	95	O	O	50	—	—	< ¼	U	25	50	U	O	50	—	—	< ¼	U	U	50
Styrene/butadiene	25	4	50	—	—	< ¼	—	—	< ¼	O	25	25	U	O	145	—	—	< ¼	U	U	95
Alkyd (med. oil)	<4	O	50	O	U	145	—	—	< ¼	O	—	<4	<4	U	25	—	—	< ¼	—	—	< ¼
Tung/phenolic	70	50	95	—	—	< ¼	—	—	< ¼	50	U	95	25	U	95	—	—	< ¼	U	O	<4

Legend: SS—slight softening. D—discoloration. F—failure. U—little or no visible effect during 7 days' contact. O—immediately affected upon contact. Numerals in columns indicate hours of exposure before attack is evident.

Stable one-can vehicles for use in baking enamels can be prepared by reacting the excess isocyanate groups with phenols or tertiary alcohols, which are reversibly removed at baking temperatures.

In Tables VI and VII the film properties of various reference paint vehicles are compared with the properties of air-drying urethane oils now under investigation in our laboratory. The method of testing chemical resistance requires comment. Films with a dry thickness of 1½ mils on glass plates after drying at room temperature for one week were placed in direct contact with the chemical reagent under an inverted jar. The spot in contact was then checked at regular intervals for visual appearance; softening of the film was estimated by prodding with a stylus. Where softening of the films is indicated in Table VII, this means only moderate softening; severe softening is rated as failure. Discoloration is regarded as evidence of chemical attack, but the films may maintain their physical integrity for a considerable period after the start of attack as shown in the table.

In this series the first four products are the oil-based urethanes, and the fifth is a commercial, polyester-based, urethane floor varnish. The other six commercially available vehicles were selected as high quality products of the types indicated.

Of the urethane oils, XP-1077 is especially interesting because, as a stable one-can system, it offers significantly improved film properties at no sacrifice of conventional handling-characteristics. The product can be pigmented in normal fashion, employs standard driers, and yields paints with satisfactory shelf-life. In many key properties it is better than standard, top-quality paint vehicles. In particular, gloss retention and durability of clear films in Weatherometer tests has been outstanding. Usefulness both as a clear varnish on exterior wood and in paints subject to contact with water is indicated.

The XP-1066/tolylene diisocyanate coatings have outstanding properties at moderate cost. The reaction of the XP-1066 and tolylene diisocyanate is carried out at controlled temperature in the presence of some xylene solvent.[1] Additional solvent is added after a holding period to gain viscosity (1–2 poise at 50% solids). The vehicle then will have a pot-life of less than 24 hrs. It is used with cobalt drier.

This XP-1066/TDI varnish is too reactive for conventional pigmentation, and it is of current interest mostly because of the remarkable properties of clear films. As a varnish over wood, the coating has truly outstanding weathering properties. Perhaps when dual-injection spray guns are worked out satisfactorily, the XP-1066/TDI system will be more broadly useful. It is a prime candidate for application in this fashion.

The XP-1093/1087 two-can system is more convenient to work with at present and has excellent film properties. XP-1093 is an oil/diisocyanate "prepolymer" with a chemical excess of isocyanate groups. The XP-1087 is a reactive catalyst added at the time of use. The chemical resistance of the cured material approached that of the polyester/diisocyanate combinations, which are handled with greater difficulty. The resistance of XP-1093/1087 to some solvents tends to be poorer than that of other urethane oils in the series. In the tables, where the softening (but not the failure) of these films by a particular chemical reagent is indicated, this softening is minor in degree and is unlikely to limit serviceability. In partcular, coatings based on these materials will be of interest for the corrosion protection of metal.

The 274 V 278 combination is an oil-based, urethane oil similar to polyester/diisocyanates in properties and indicated cost level. Films are much harder than those obtained from other vehicles, and this hardness is gained at a minimum sacrifice in toughness.

From the tabulated data it is apparent that no single material has a monopoly on all virtues. It is also apparent that the urethane oils must not be regarded as a single entity. Rather they encompass a broad group of materials ranging from fast-drying to slow-drying coatings materials, containing some products with superior weathering properties, some with good electrical resistance, some with outstanding hardness and chemical resistance. Coatings tailored to meet particular service requirements can be made by the urethane reaction. Plasticizers, adhesives, foams, potting compounds, and molding materials also can be made in this fashion. With such a versatile system at hand, rewarding prospects for research and development are apparent.

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The Influence of Autoxidation on the Chemical Assay of Cholesterol[1]

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MANY WORKERS specify specially purified cholesterol for use as a standard for analytical procedures (1–6). This stems from the known instability of cholesterol under some conditions of exposure to light and air (1, 2, 7, 8a), the crystallization of cholesterol as a hydrate from some solvents (8b, 9), and the presence of steroid impurities in commercially available cholesterol (8c, 10–14). Since most analytical procedures for cholesterol employ the relatively nonspecific Liebermann-Burchard reaction, it was desired to ascertain what influence such factors as long storage, autoxidation, and steroid impurities might have on the suitability of a sample of cholesterol for use as a standard for assay purposes.

Recently Sperry and Brand (15) reported losses of up to 25% of cholesterol when assaying "dried" serum lipides which had been exposed to air. The losses were attributed by these authors to oxidative degradation although the partial insolubility of the lipides also reported occurring under those conditions may have been causative. It was one of the purposes of this study to autoxidize cholesterol directly by a proven procedure and then to observe the effects on the chemical assay of cholesterol by standard methods.

Cholesterol autoxidation and factors governing it have been studied in detail by Bergström and Wintersteiner (16–20). Since the reaction mechanism proposed by these authors involving intermediary formation of a hydroperoxide group on a methylenic carbon atom α to the double bond is similar to the mechanism proposed by others (21) for autoxidation of methyl oleate, it was desired to test whether or not linoleate would propagate the autoxidation of cholesterol as has been noted (22) to be the case for oleate. This consequence would be of importance in assay work since cholesterol occurs in biological materials accompanied by polyunsaturated fatty acids, either as the ester or as companion mixed lipides. The suggestion of Fieser (13) that an unsaturated companion-sterol of cholesterol might be autoxidized by action of lard peroxides on it lends support to this possibility. As a part of the study being reported here, the influence of linoleate on the autoxidation of cholesterol in organic solvent, in lipide films, and in the colloidal system described by Bergström and Wintersteiner is being studied in this laboratory.

Materials and Methods

The cholesterol samples used are described in Table I.

TABLE I

Cholesterol Samples[a] Used

Designation	C-1	C-2	C-3
Description	Merck, U.S.P.[b]	Eastman Kodak Co. Cat. No. 909	Purified cholesterol[c]
Melting point, °C	145.5–146.5	144.5–146	146–147
Specific rotation in chloroform $[\alpha]_D^t$	−42°, −41°	−41°, −43°	−38°, −39°
t	29, 30.5	28, 27.5	31.5, 32.5
C in %	1.06, 1.04	1.15, 1.01	1.10, 1.15
Analysis—$C_{27}H_{46}O$ Calculated: C 83.86, H 11.99	—	—	C 84.01, H 11.93 C 83.93, H 12.02

[a] All melting points are uncorrected. Microanalyses and optical rotations are by E. W. D. Huffman, Denver, Colo.

[b] This sample had been stored in an amber bottle at room temperature in the laboratory for more than two years.

[c] Cholesterol (C-2) was brominated by the Windaus (23) procedure as modified by Schwenk and Werthessen (24). The dibromide was recrystallized twice, m.p. 115°C., from ethylene dichloride and then debrominated by the method of Fieser as described by Schwenk and Werthessen (24). The recovered cholesterol was recrystallized three times from absolute methanol without change in m.p., 146–147°C.

Recovery of Cholesterol Following Refluxing with Organic Solvent in the Presence of a Readily Autoxidizable Lipide Substrate. Two standard solutions in ethanol-ether (3:1 v/v) were prepared, one of corn oil (Mazola) and the other of cholesterol (C-1). Suitable aliquots of the solutions were placed in separate flasks so as to permit refluxing of the cholesterol solution, cholesterol solution plus corn oil solution, and corn oil solution. Following a reflux period of 4 hrs. under Allihn condensers open to the atmosphere, the flask contents were analyzed in duplicate for total cholesterol by the Sperry and Webb (1) modification of the Schoenheimer and Sperry (3) method and compared with a similar analysis of an unrefluxed control of the standard cholesterol solution.

Autoxidation of Cholesterol in Aqueous Colloidal Suspension. Cholesterol (C-1) in aqueous colloidal suspension stabilized with sodium stearate was autoxidized for 3½–4 hrs. by aeration according to the "standard conditions" described by Bergström and Wintersteiner (19) at pH 8.2. Two 25-ml. aliquots of mother liquor were removed at zero time and again, following the 3½- to 4-hr. aeration period. These aliquots were acidified and analyzed for total lipide, diols,[2] and ketone by methods described by Bergström and Wintersteiner (19). The lipide extracts of the aliquots were analyzed for cholesterol (both free and total) according to the Sperry and Webb modification (1) of the Schoenheimer-Sperry (3) method, also by simply applying the Liebermann-Burchard color reaction with the reagent and conditions of Sperry and Webb (1) and alternatively of Abell *et al.* (5) for color development. Infrared

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[2] The color produced by the chromogenic diols, using the Lifschütz reaction, was measured at 620 mμ. The S-62 filter used by Bergström and Wintersteiner in the Zeiss step-photometer had a maximal transmission at 619 mμ (25).