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Isocyanate-Modified Drying Oils

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THE FIELD of isocyanate chemistry and urethane polymers has held the interest of paint formulators and resin chemists increasingly in recent years. Because of their extreme reactivity, isocyanates can be used in coatings in an almost unlimited number of ways. Recently Remington and Lorenz (1) have listed four distinct types of urethane-coatings systems. These are as follows.

1. A two-component system in which an isocyanate polyol adduct of low volatility is mixed with an hydroxyl-containing resin just prior to use. The polyhydroxy material might be a polyester, a polyether glycol, or castor oil. This is, of course, a two-package system, which has a limited pot life once the two components are mixed. It can be pigmented by dispersing the pigments in the polyhydroxy component. By varying the amount of hydroxyl groups and the amount of isocyanate available for cross-linking, the formulator can achieve a wide range of physical properties in the finished film. This system can be formulated to give outstanding chemical resistance.
2. A one-component system consisting of two ingredients, an isocyanate polyol adduct which has been "blocked" to make it nonreactive, and a polyhydroxy resin. Upon baking, this blocking agent (usually phenol) is driven off, and the isocyanate is available for cross-linking. This system is stable and can be pigmented. It must be cured by heat.
3. A one-component system consisting of an isocyanate-terminated polymer, which cures by reaction with atmospheric moisture. This system is stable as long as no moisture is present. It is extremely difficult to pigment since moisture-free pigments must be used. Once the package has been opened and air with some moisture enters the container, shelf life is limited. A variation of this system provides for the addition of an amine catalyst prior to use. This then becomes a two-package system.
4. The so-called oil-modified urethane system, or urethane oil. Here the isocyanate is reacted with a partial ester of a polyol with an unsaturated fatty acid or an alcoholysis product. If the amount of isocyanate used is stoichiometrically equivalent to the hydroxyls present, the resulting resin is stable. This system cures by the conventional mechanism of polymerization through the unsaturation in the fatty acids. This is a stable system which can be pigmented and handled in much the same manner as conventional-coatings resins.

These so-called isocyanate-modified oils were among the first urethane materials to find any practical industrial applications. A development of pre-World War II German urethane chemistry, these urethane oils were used in war-time Germany as protective coatings and were reported in the BIOS and PB reports published shortly after the war as being closely related to alkyd resins in formulation and in properties. Since that time relatively little attention has been given to products of this type. In 1951 Robinson and Waters (2) described an extensive study of urethane oils, which closely followed the earlier German work. More recently Pansing (3) reported on similar products based on linseed oil and soybean oil. Apart from these contributions, little detailed information has appeared in the literature.

Chemistry

The isocyanate group will react with and add to any compound containing an active hydrogen. This would include water, alcohols, primary and secondary amines, carboxylic acid groups, hydrogens, or certain activated methylene groups, such as aceto-acetic ester or malonic ester, etc. The urethane reaction, of course, refers specifically to the reaction of the isocyanate group with alcohols.

When a polyisocyanate is reacted with a polyhydroxyl material, a urethane polymer is the result. As shown in Figure 1, when a di-isocyanate (*e.g.,* tolylene di-isocyanate) is reacted with either a partial ester of a polyol (*e.g.,* glycerine) and a drying oil fatty acid, or the product of the alcoholysis of the drying oil with the polyol, the resulting product may be designated as an oil-modified urethane polymer. The analogy with an alkyd resin (which is, in reality, an oil-modified polyester) is obvious. Also obvious is the comparison with an epoxy ester, which is an oil-modified polyether.

There are however great differences between these materials. Table I shows a comparison of properties among a glycerine alkyd, an urethane oil, and an epoxy ester all modified with 59% linseed fatty acids. While one might expect similarities, especially in regard to the alkyd, the differences are striking. The viscosity of the alkyd is A, that of the urethane, Z. The drying properties are also quite dissimilar. The urethane dries to a tack-free film in 40 min. as against two hours for the epoxy ester and five to six hours for the alkyd. The urethane reaches a Sward Hardness of 34 in one week, as against 12 for the alkyd, and 18 for the epoxy ester.

TABLE I

Comparison of an Alkyd, Epoxy Ester, and an Urethane Oil

	Alkyd	Epoxy	Urethane
Linseed F.A.	59	59	59
Glycerine	17	....	16
TDI	....	....	25
Epoxy	....	41	....
P.A.	24	....	....
Solids	50%	50%	50%
Solvent	Xylol	Xylol	Xylol
Viscosity	A	C	Z
Set to touch	2 hr.	1 hr.	20 min.
Tack-free	5–6 hr.	2 hr.	40 min.
Dry-through	8–10 hr.	12 hr.	2 hr.
Sward 1-wk.	12	18	34

These differences between oil-modified alkyds and oil-modified urethanes of equal oil-length can perhaps best be explained by a close examination of the reactions that can take place during the formation of the respective resins. Seavell (4) has recently discussed the reactions which might take place during alkyd formation. These are a) esterification between the alcoholysis product and the dibasic acid, b) C_{18} chain polymerization, that, is, bodying of the oil portion; c) interesterification, either alcoholysis or acidolysis; d) etherification, which can take place during esterification as well as during alcoholysis.

The reactions which might take place during the formation of an isocyanate oil would be a) urethane formation between the isocyanate and the hydroxyl groups, b) reaction of the isocyanate with any free fatty acids, c) allophonate formation, that is reaction of the isocyanate with already-formed urethane groups, and d) dimerization of the di-isocyanate by addition. It would seem unlikely that these last two reactions would take place to any great extent under the reaction conditions without a catalyst. Likewise the reaction conditions would preclude any extensive polymerization of the fatty acids present. Nor would one expect any significant amount of free fatty acid to be present in the alcoholysis product. The urethane reaction then is probably the only one of any importance. Thus it would seem that these differences are perhaps best explained by our incomplete knowledge of the extent of the other reactions which take place during esterification in alkyd manufacture. Such things as formation of cyclic products of relatively low molecular weight might account for the evident difference in polymer size of the alkyd *versus* the urethane. Then too it is probable that the urethane reaction goes much farther toward completion than the alkyd.

Preparation

As previously mentioned, the urethane oil could be made by reacting the di-isocyanate with either a partial ester or an alcoholysis product. A typical procedure might be as follows. Heat 75 g. of heat-bodied linseed oil and 6.5 g. of glycerine with 0.2 g. of calcium naphthenate (4%) to 482°F. under an inert atmosphere and hold for 2 hr. to complete transesterification. Cool to 122°F. and add 18.5 g. of TDI slowly over a 30-min. period, allowing the temperature to rise to 140°–150°F. Solvent must be added as the viscosity increases. When all of the xylene (100 g.) is added, hold for viscosity of Q-S at 50%.

Formulation Variables

From the above procedure one can readily see what some of the formulating variables are, *e.g.*, choice of oil, choice of polyol, amount of TDI, viscosity of the starting oil, etc. It will be the purpose of the next part of this paper to explore the effects of some of these variables.

TABLE II

Linseed and Soybean Urethane Oils

	Refined LSO	G-H viscosity LSO	LSO alkyd	Refined SBO	G-H viscosity SBO	SBO alkyd
Mol ratio PE/Oil.	0.8	0.8	....	0.8	0.8	....
% Equiv. TDI	100	90	....	100	90	....
Viscosity	Y	Z6	....	X	Z5–Z6	....
% Solids	60	60	....	60	60	....
% Free NCO	Trace	0	....	Trace	0	....
Dry (hrs.)	1½	2¾	2¾	2¾	4¾	3¾
Sward hardness						
1 day	18	15	15	14	8	15
7 days	32	19	29	18	10	18
14 days	39	21	34	20	10	23
Flexibility	ok	ok	ok	ok	ok	ok

Data are shown in Table II for the preparation of four products based on linseed and soybean oil with pentaerythritol and tolylene di-isocyanate. The tolylene di-isocyanate used in all reactions described in this report was the commercially available mixture of 80% 2-4 isomer and 20% 2-6 isomer. Using both linseed and soybean oils, one product was prepared with alkali-refined oil and another was prepared by using a prebodied or polymerized oil which was obtained by heating alkali-refined oil in an inert atmosphere at a temperature of 500°F. until the viscosity reached G-H on the Gardner-Holdt scale. The amount of pentaerythritol was based on preliminary experiments, which had shown that when the ratio of polyol to oil is substantially less than that used here difficulty was encountered with films tending to "top dry," that is, the film would oxidize rapidly on the surface but would remain relatively soft underneath for an extended period of time. The amount of TDI used with the alkali-refined oils was equivalent to the PE present in the composition. TDI used with prebodied oil products was held to 90% of the equivalent amount because of the relatively high viscosities obtained.

In each instance the preparations followed the same general pattern. The refined or pre-bodied oil was heated with the PE at a temperature of 480°F.

TABLE III

Film Properties of Linseed Urethane Oils

	Gly.	Gly.	Gly.	PE	PE	PE	MG	MG	MG
Mol ratio polyol/oil	1.2	1.55	2.1	0.9	1.0	1.2	0.62	0.75	0.86
% Equivalent TDI	79	79	72	81	80	74	90	84	80
Weight % TDI	19.9	23.8	26.9	20.1	21.7	23.0	16.3	17.7	19.2
Dry (hrs.)	2	1¼	1	1½	1	1	2	1¾	1½
Sward hardness									
1 day	8	17	20	10	16	20	10	16	21
7 days	20	29	30	25	30	33	24	30	33
14 days	24	40	42	31	39	41	31	36	38
Impact	>28	22	10	12	6	4	>28	>28	20
3% NaOH hrs. to failure	1¼	6	6½	3½	5½	8	1½	3½	4

Gly. = glycerine. PE = pentaerythritol. MG = methyl glucoside.

in the presence of an interesterification catalyst for a period of 1 hr. The product was cooled and mixed with mineral spirits and reacted with TDI in an inert gas atmosphere at a temperature of 200°F. with constant agitation for 2 hr. The percentage of free NCO remaining in the product at the end of the reaction period was determined by the standard analytical procedure, using di-N-butylamine.

Solutions of the urethane oils at 50% solids in mineral spirits were prepared with 0.05% cobalt and 0.4% lead driers. These were compared with a medium oil-length linseed alkyd and a medium oil-length soybean alkyd for dry, hardness, and flexibility characteristics. As is shown in Table II, both the linseed and soybean urethane products prepared from refined oil dried more rapidly than the comparable alkyds and both developed hardness equal to the alkyds upon air-drying over a 14-day period. The products prepared from pre-bodied oils dried more slowly and developed only approximately one-half the hardness shown by the refined oil products. All of the urethane oils as well as the alkyds showed satisfactory flexibility chracteristics when panels were bent over a ⅛-in. mandrel after aging for 5 days at 122°F.

Another series of urethane oils was prepared by using alkali-refined linseed oil with varying levels of glycerine, PE, and methyl glucoside as polyols. The purpose of this work was to check film properties of oils prepared with relatively high levels of polyols, thus reducing the amount of triglyceride in the final product, and to determine the effect of the kind of polyol on film properties.

Preparation of the products in this series differed from those described previously in that the alcoholysis reaction was continued for 2 hr. at 480°F., and reaction with TDI was carried out in steps, that is, the alcoholysis product was reacted initially with one-half the amount of TDI equivalent to the polyol in the presence of a sufficient quantity of mineral spirits to yield 45% solids solution. After allowing the initial charge of TDI to complete its reaction, additional quantities of TDI were added in small increments with corresponding additions of spirits until the reaction mixture attained a viscosity of D to H at 45% solids. The temperature was maintained at 200°F. throughout the reaction. One hour was allowed between additions for the reaction of the TDI to go to completion.

Three products were prepared with each polyol, and these were compared for dry time, Sward hardness, impact resistance, and resistance to caustic soda solution.

Reverse impact values were determined by using the variable impact tester on films cast on steel panels after a 21-day air-dry period. Caustic resistance was measured by a conductivity method described by Bratt (5).

The mol ratio of polyol to oil, percentage equivalent TDI and weight per cent TDI used in these preparations are shown in Table III along with data obtained from evaluation of the films. It will be noted that with the glycerine and PE preparations, in which relatively high mol ratios of polyol to oil were used, the amount of TDI required to reach viscosity was relatively low, ranging from 72 to 81% of theoretical. The methyl glucoside products prepared with a lower ratio of polyol to oil required reaction of 80 to 90% of the equivalent TDI to obtain the desired viscosity characteristics.

Dry-time data show that the products based on PE exhibited a more rapid rate of dry than those prepared with the other polyols. The two products prepared with the higher mol ratios of PE to oil as well as the product based on the highest mol ratio of glycerine appeared to show drying characteristics similar to lacquers, *i.e.*, the rate of evaporation of solvent was the governing factor rather than the rate of oxidation of the film. With the products in which lower mol ratios of polyol to oil were used, the drying rates were roughly proportional to polyol and TDI contents.

The Sward hardness data show that films comparable in hardness characteristics were obtained from all three polyol systems. Comparison of the products in each polyol series prepared with the higher levels of polyol and TDI shows relatively little difference in hardness despite the variation in polyol and TDI content. This suggests that the limiting factor in determining film hardness is the extent of oxidation as determined by the unsaturation of the oil rather than the polymer composition. It will be noted that the methyl glucoside oils showed Sward hardness values approximating those of the other polyol products although they were prepared with lower ratios of polyol and TDI.

The reverse impact values obtained with the PE products were uniformly low as compared to oils based on the other polyols. The relatively higher values obtained with the methyl glucoside products were, no doubt, influenced by the presence of appreciable amounts of triglyceride in the final product since these oils were prepared by using comparatively low mol ratios of polyol to oil.

The films of the PE and glycerine products prepared with the higher modification of polyol and TDI showed excellent caustic resistance. The methyl glucoside products were somewhat less effective in this respect. This can also be related to the lower polyol and TDI content of the methyl glucoside materials.

TABLE IV

Properties of Some Commercial Urethane Oils

	A	B	C
Solids (%)	50	60	50
Solvent	M/S	Xylol	Xylol
Viscosity	Z_1–Z_2	Z_1–Z_2	Z_1–Z_2
Set to touch	40′	6′	10′
Tack-free	75′	15′	20′
Hardness 24 hrs	2B	5B	4B
Hardness 7 days	B	HB	HB
Hardness 30′ at 300°F.	F	H	H
Impact air-dry (inch lbs.)	160	144	160
Impact bake (inch lbs.)	160	160	160

Samples A, B, and C are Cargill polyurethanes 101, 1210, and 1220, respectively. Same designations are used in other tables.

In addition to these formulation variables, other possibilities can be conjectured. For instance, the substitution of a polyether glycol for some of the polyol has been suggested (6). In effect, this would produce a kind of graft polymer. It is claimed that such products have excellent speed of dry.

Properties

Table IV shows the specifications and drying characteristics of some commercial oil-modified polyurethanes. One of the most impressive properties of these products is their rapid dry, much faster than alkyds or other more conventional coatings resins. Also, while these films harden somewhat slowly, the ultimate hardness is exceptional for air-dry materials, especially in view of the excellent flexibility and impact resistance. Mar resistance, a difficult property to measure but nevertheless a very important property, is one of the outstanding characteristics of these resins.

Abrasion resistance of urethane coatings has generally been reported to be outstanding. That this is also true of the oil-modified urethanes can be seen in Table V. Whether measured by the falling sand method or by the Taber Method the urethane oils compare quite favorably to other materials which are known to have good abrasion-resistance. This excellent wear-resistance has also shown up in field tests in both clear and pigmented films.

TABLE V

Abrasion Resistance

	Taber index	Falling sand (MG loss/liter)
Urethane oil A	35	.076
Urethane oil B	95	.075
Urethane oil C	96	.087
Commercial epoxy ester No. 1	164	.107
Commercial epoxy ester No. 2	103	.108
Reactive urethane vehicle	76	.091

Taber—CS-17 wheel—1,000- gm. weight. Sand—No. 2 Ottawa.

As to resistance to water, solvents, and chemicals Table VI gives a summary of some comparative results obtained by many series of tests. For the most part, our resistance tests are performed in one of two ways, either by coating one-inch steel probes with the resin under study and immersing the probes in the test solution or by using the Bratt conductivity cell. The salt spray testing was done in a conventional salt fog cabinet according to A.S.T.M. standards.

In general, the oil-modified urethanes are superior to alkyds and epoxy esters in regard to solvent resistance and water resistance. Their superiority over the alkyds in water resistance is, of course, quite marked. As to alkali resistance, while the urethanes represent a significant improvement over alkyds, they are usually somewhat poorer than the better epoxy esters.

TABLE VI

Water and Chemical Resistance

	Solvent resistance	Distilled water @ 100°F.	Wooden panels in water	3% NaOH, air-dry	3% NaOH, baked	Salt spray
Urethane oil A	G	G	G	F	F	F
Urethane oil B	G	G	E	F	G	E
Comm. epoxy ester No. 1	F	G	F	G	G	F
Comm. epoxy ester No. 2	P	G	G	G	G	G
Medium linseed alkyd	F	P	P	P	P	G
Reactive urethane type 3	E	G	E	E	....	....

Perhaps the most difficult property of any coatings material to measure is exterior durability. Based on panels exposed over a period of several years in Minneapolis, Florida, and Arizona as well as in accelerated weather testing, the over-all durability pattern of oil-modified urethanes is becoming clear. In general, pigmented urethane films tend to lose gloss and chalk at a somewhat earlier point than good oil-modified alkyds. However ultimate durability seems to be as good as alkyds. For example, a series of oil-modified urethanes exposed at Minneapolis showed less gloss and slightly more chalk at one year than the control, a medium soybean oil alkyd. At the end of three years however all of the panels are chalking at a comparable rate. The urethanes show no tendency toward checking, cracking, or loss of adhesion. Panels exposed at 45° in Florida follow this same pattern. Recently however one urethane indicates a possible improvement in gloss retention. At 10 months, it is somewhat better than the alkyds.

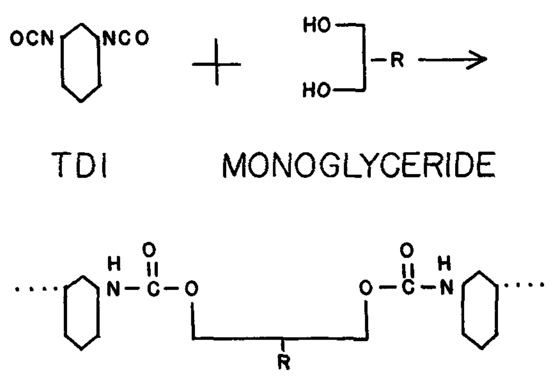

FIG. 1. Oil-modified urethane polymer idealized structure.

Conversely the durability of unpigmented films of the oil-modified urethanes is far better than alkyds and other more conventional coatings materials. The results of one series of Weatherometer tests are shown in Table VII. The advantage of the urethanes is quite noticeable. Test-fence exposures in Minneapolis and Arizona seem to follow the same general pattern.

The combination of interesting properties which these urethane oils have has already led to their use

TABLE VII

Accelerated Weathering

	450 hrs.	575 hrs.	775 hrs.
Urethane oil A	ok	ok	ok
Urethane oil B	ok	ok	ok
Alkyd	ok	Slt. check whitening	Failed
Epoxy ester	Slt. check low gloss	Severe whitening	Failed
Spar varnish	Checking	Failed	....

in several areas in the coatings industry. For example, exterior durability together with water resistance has led to their use in spar varnishes. Speed of dry and wear resistance have suggested their evaluation and use in both clear and pigmented floor finishes. Similarly impact resistance, adhesion, solvent holdout, and salt spray-resistance have brought about the use of the urethanes in some metal primer applications. As new resin-formulating data become available, and, as more is learned about paint formulation techniques with these resins, it is likely that oil-modified urethanes will attain a significant use in the coatings industry.

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Autoxidation and Autoxidative Polymerization

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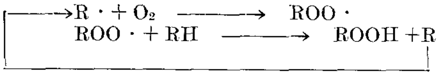
IN THE OXIDATION of drying oils, as in the preparation of blown oils and the formation of films, the reactions that lead to hydroperoxide formation are usually referred to as autoxidation. The subsequent reactions of the peroxides that give polymers are termed autoxidative polymerization. The over-all process is extremely complex because both reactions have many ramifications and go on simultaneously.

Autoxidation

Primary Reaction. Autoxidation has been studied most extensively with methyl oleate and linoleate at low temperature. Unsaturated hydroperoxides, the primary reaction products of these esters, are formed in an autocatalytic chain reaction in accordance with the following mechanism:



$$\begin{aligned} R\cdot + O_2 &\longrightarrow ROO\cdot \\ ROO\cdot + RH &\longrightarrow ROOH + R\cdot \end{aligned} \qquad (2,6)$$

Triunsaturated hydroperoxides have been isolated in yields of about 60% from autoxidized methyl linolenate (27) and likewise are the primary products of the autoxidation of this ester.

Although the mechanism of the primary reaction is well defined, there are certain facets of the autoxidation of nonconjugated fatty acid esters that need further clarification, particularly the mode of initial attack by molecular oxygen or the initiation of the chain reaction, and the formation of products other than the simple hydroperoxides.

Chain Initiation. The reaction involved in the initiation of the chain reaction is difficult to analyze because theoretically only a single molecule need be involved. This eliminates product analysis as a means of examining this stage of the reaction. At the time of the development of the hydroperoxide theory of autoxidation (6, 12) it was postulated that the reaction involved an initial attack by molecular oxygen. There was considerable speculation whether the site of the initial attack was at the double bond or at the methylenic carbon atom adjacent to the double bond.

The theory of initiation by direct oxidative attack was based primarily on the observation that, on extrapolation of the plot of the rate of autoxidation *vs.* the extent of the reaction, the curve did not pass through the origin but gave a positive intercept of the rate of oxidation axis (6), indicating that a minor but significant reaction took place prior to the primary reaction. This was presumed to be the initiation reaction. However detailed studies by Bateman *et al.* (3, 4) showed that the relationship between the rate and extent of autoxidation deviated from linearity in the early stages of autoxidation and, in fact, intersected the origin; hence the extrapolation upon which this hypothesis was based was invalidated. These investigators demonstrated further that the deviation of this relationship from the linear in the initial stage of autoxidation resulted from a difference in the mode of peroxide decomposition at this stage of the reaction. At low peroxide concentrations the reaction was first order whereas at high peroxide concentrations it was bimolecular because of association of the hydroperoxides. This hypothesis was supported by infrared spectral data which showed that hydroperoxides became associated very easily. It was hypothesized that initiation of the chain reaction took place essentially as a result of peroxide decomposition. Formation of the initial hydroperoxides was not explained, but it was considered to be of such a small order as to be insignificant.

Uri (39) advanced the hypothesis that the initially formed hydroperoxides, as well as the first order decomposition of hydroperoxides leading to the initiation of the chain reaction, occurred as a result of metal catalysis. This view was based on extensive kinetic studies as well as the observation that even the purest fatty acid ester preparations contained traces of metal catalysts.

Formation of Nonhydroperoxidic Material During Autoxidation. There is some evidence that nonhydroperoxidic substances are formed concurrently with the primary reaction in the autoxidation of nonconjugated fatty acid esters. This has been demonstrated in the autoxidation of methyl oleate at various stages