ricinoleic acid with the DCO acids obtained in a previous batch. Under the influence of heat the DCO acid is split off with the removal of an adjacent hydrogen to form an additional DCO acid. In actuality a mixture of conjugated and nonconjugated acids would be used for esterification and obtained by the reaction. Also some estolide formation could not be avoided.

DCO acids may also be prepared by saponifying and splitting DCO. This is at present the preferred method for commercially preparing the acids. The better grades are further refined by distillation.

A good grade of DCO acids contains about the same mixture of linoleic isomers (*cis* and *trans*, conjugated and nonconjugated) discussed under the oil except that there are probably fewer estolides present. Since castor oil is 90% ricinoleic plus a small amount of natural linoleic, the resultant DCO acids would be very nearly pure linoleic acids. Spectrophotometric diene values indicate that the acids have a slightly higher percentage of the conjugated isomer.

A.S.T.M. has recently issued the following tentative specifications for dehydrated castor acids (D-1539-58T):

	Type I	Type II
Acid value	195–200	187–195
Saponification value	195–200	193–199
Iodine value	150–156	138–143
Color (Gardner)	1 max.	5–8
Spectrophotometric diene value	28–35	25–32

Type I is the distilled DCO acids, and Type II is undistilled.

The characteristic feature of the top grade DCO fatty acids is that they are composed almost entirely of dienoic acids, accompanied by negligible amounts of nondrying acids and no acids with three double bonds. Thus excellent drying alkyds with little yellowing tendency may be prepared. No aftertack has been observed in the alkyds made with the acids. Since the acids are more expensive than the oil, they are used principally when some special property is desired. The less expensive undistilled acids may be used where darker color and slower bodying characteristics are permitted.

DCO acids are used to modify epoxy resins (reaction products of epichlorohydrin and bisphenol). The epoxy resin functions as a high-molecular-weight polyalcohol which esterifies the fatty acids to form esters. As an example of the preparation of these esters, 60 parts of epoxy resin (Epon 1004, Shell) and 40 parts of DCO Acids 9–11 Acids, The Baker Castor Oil Company) are cooked in an inert gas at 500°F. to an acid number of 2. It is thinned to 50% solids with xylene. 0.04% cobalt is added for air-dry and 0.005% cobalt for baking. It is designed especially for use with urea or melamine resins in the formulation of low-bake metal finishes. In air-dry applications, while not suitable for brushing, it may be sprayed or dipped and will reach the tack-free state in 2–3 hrs. The principal purpose of the fatty acid modification is to produce the desired flexibility without lessening the excellent properties imparted by the heat-converted epoxy resin. Undistilled DCO acids are sometimes used because of the price advantage and faster esterification rate. However the distilled acids are preferred for good color, maximum baking speed, and optimum chemical resistance and toughness.

REFERENCES

1. U. S. Dept. of Agriculture, Circular FFO-2-59 (1959).
2. Cannon, D. R., editor, Chem. Eng., *66*, No. 12, 88, 90 (1959).
3. Rassow, B., Angew. Chem., *26*, 316 (1913).
4. Fokin, S., J. Russ. Phys. Chem. Soc., *46*, 224–226 (1914).
5. Fokin, S., J. Russ. Phys. Chem. Soc., *46*, 1027–1042 (1914).
6. Scheiber, J., Farbe u. Lack, *1928*, 518–520 (1928).
7. Ufer, H., German Patent 529,557 (1931).
8. Ufer, H., U. S. Patent 1,892,258 (1932).
9. Colbeth, I. M., U. S. Patent 2,392,119 (1946).
10. Radlove, S. B., *et al.*, J. Am. Oil Chemists' Soc., *25*, 268–271 (1948).
11. Forbes, W. C., and Neville, H. A., Ind. Eng. Chem., *32*, 555–558 (1940).
12. Terrill, R. L., J. Am. Oil Chemists' Soc., *27*, 477–481 (1950).
13. Boeseken, J., and Hoevers, R., Rec. trav. chim., *49*, 11655–11658 (1930).
14. Priest, G. W., and Mikusch, J. D. v., Ind. Eng. Chem., *32*, 1314–1319 (1940).
15. Chowdhury, D. K., and Mukherji, B. K., Proc. Nat. Inst. Sci. India, *22A*, 199–203 (1956).
16. Mikusch, J. D. v., Paint Manuf., *25*, 386–391 (October 1955).
17. Bolley, D. S., J. Am. Oil Chemists' Soc., *30*, 396–398 (1953).
18. Patton, T. C., Official Digest, No. 326, 177–202 (March 1952).
19. Patton, T. C., Official Digest, No. 368, 627–636 (September 1955).
20. Terrill, R. L., Paint, Oil, and Chem. Rev., *116*, No. 4, 13–14, 14B, 32 (1953).
21. Patton, T. C., and Lindlaw, W., Paint and Varnish Prod., *44*, No. I, 21–29, 72 (January 1954).
22. Rowe, R., Paint Technology, *19*, No. 210, 79–83 (1955).

Copolymer Drying Oils

R. F. HELMREICH, Coatings Technical Service, Dow Chemical Company, Midland, Michigan

The copolymer drying oils grew out of the discovery that vegetable oils could be modified with natural resins, resulting in improved properties. The discovery must have been greeted with cheers by early formulators. Drying oils were despairingly slow in drying and were soft. The natural hard resins, used alone, were entirely too brittle to be practical. It was a happy chance that resulted in a compromise of many good properties of both oil and resin by the simple expedient of heating to induce compatibility. As the demand for oil-modified resins increased, synthetic resins were substituted for the natural because of the latter's limited supplies and erratic quality. Oil-modified phenolics and alkyds were the result.

The uses for oil-modified resins became diverse, and requirements became more severe. The market demanded lower cost, improved color, and faster drying. These needs could be met by modifying oil-alkyd systems with vinyl monomers. Indeed it was later found that the oil itself could often be successfully modified with the vinyl monomer alone, and the vehicle resulting from such modification fits the title, a copolymer drying oil.

Preparation of the Copolymer Oil. For purposes of this paper, we shall define a drying oil as any vegetable oil, drying or nondrying which is useful in preparing protective-coating vehicles. The reason for including nondrying oils will be apparent later.

In theory any unsaturated material can be made to react with vegetable oils. This includes the styrene family, the vinyls, acrylics, cyclic olefins, and maleic anhydride. In practice modification is largely limited to monomers of the styrene family. For simplicity let us narrow our field for the moment and consider only vinyltoluene. This reactive monomer permits great latitude in the selection of the vegetable oil. With a given oil, vinyltoluene may be reacted in a wide range of concentrations to achieve several combinations of properties.

The classical preparative method for modifying vegetable oils with monomer involved cooking all of the ingredients, with or without solvent and catalyst. This is giving way to the continuous addition method, where monomer and catalyst are mixed and added to the heated oil and solvent gradually, with stirring. Control over the course of the reaction is exercised simply by varying the rate of monomer addition. Further a second monomer or additional catalyst may be added at some experimentally determined optimum time during the cook.

Properties of the Copolymer Oil. Monomer modification and the accompanying process variables bring a variety of new properties to vegetable oils:

Viscosity—increased by monomer modification, approximately in proportion to concentration of the monomer used. For a given ratio of monomer to oil, a lower temperature, lower concentration of cooking solvent, and high concentration of catalyst all promote high viscosity (Figures 1, 2, and 3) (1, 2). The effect of divinylbenzene monomer on viscosity deserves special mention. With two vinyl groups on the benzene ring, it promotes crosslinking and increases viscosity rapidly. However copolymers containing divinylbenzene are of only slight commercial significance because the resulting viscosity is difficult to control, and the vehicles tend to gel in storage.

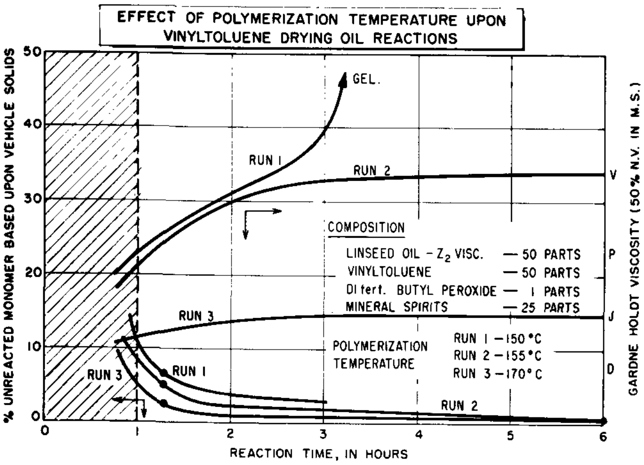

FIG. 1. Effect of polymerization temperature upon vinyltoluene drying oil reactions.

Dry Time—reduced by monomer modification (3). Better to understand this, one may think of the copolymer vegetable oil, in the reverse sense, as an oil-modified, vinyl polymer lacquer. This is truly the situation when a nondrying oil, such as coconut is used. This saturated oil becomes simply a chemically-bound plasticizer. Removal of the solvent leaves a film with near ultimate hardness, and this behavior is characteristic of lacquers. With a drying oil, such as linseed oil, oxidation eventually contributes to film properties, but evidence of the polymer lacquer character of the vehicle will always be seen in the dry time of the film except when the monomer/oil ratio is very small.

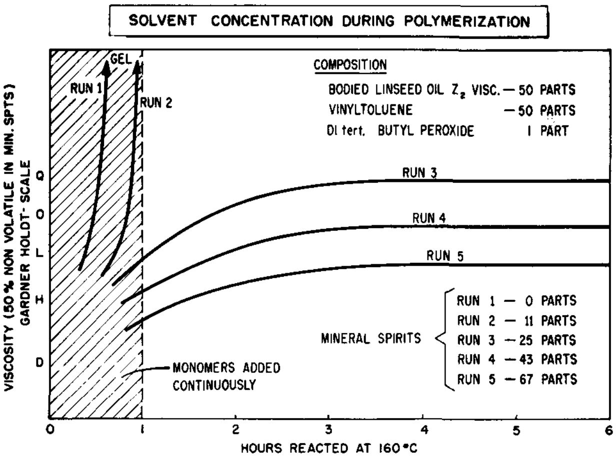

FIG. 2. Solvent concentration during polymerization.

Flexibility—adequate and controllable. The vegetable oil serves as an excellent plasticizer for the normally brittle polymer lacquers. For a given application the monomer/oil ratio can usually be balanced to give both the desired rate of dry and the desired flexibility.

Color—usually improved by monomer modification. All monomers commonly used with vegetable oils are almost water-white. The moderate cooking temperature need not contribute greatly to yellowing, either of monomer or oil, so that the reduction in color is approximately proportional to the monomer concentration in the copolymer.

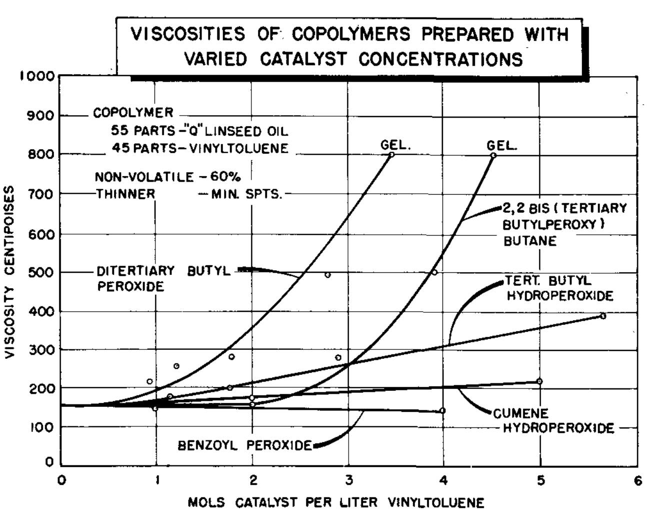

FIG. 3. Viscosities of copolymers prepared with varied catalyst concentrations.

Gloss—improved by monomer modification. A styrene polymer lacquer dries rapidly to an excellent gloss. As expected then, the improvement in the gloss of copolymer vegetable oils, over the oils themselves, is in direct proportion to the extent of monomer modification.

of the styrene family are often less costly than the vegetable oil, but to this must be added catalyst and processing costs.

Price—comparable to that of the oils themselves. Monomers

Not all of the property changes brought by monomer modification are desirable:

Weather Resistance—may be decreased by monomer modification. Styrene or vinyltoluene at 30–35% monomer maintains weather resistance comparable to that of oil alone. But higher levels of modification often lead to excessive chalking and checking.

Solvent Resistance—sometimes poor. Styrene and vinyltoluene modified oils in particular have reduced solvent resistance, but this can often be corrected by additional modification with a second monomer. For example, oils modified with acrylonitrile and vinyltoluene show fair gasoline resistance.

Chemistry of Monomer Modification

What is the nature of the reaction between vinyl monomer and vegetable oil? This is a question that has occupied the attention of coatings chemists since before 1940. The consensus denies a single clean-cut reaction product, concluding that monomer modified oils are complex mixtures.

Three types of catalysts, acidic, basic, and free radical, can theoretically bring about the reaction of monomers with drying oils. For practical purposes we may restrict ourselves to the free radical types, both added hydroperoxides and peroxides, and the spontaneous autoperoxides in the oil.

The nature of the reaction initiated by free radicals is still open to question. Hewitt and Armitage (4) made a serious attempt to explain the vinyl monomer/drying oil reaction. Finding conjugated vegetable oil double bonds conducive to a homogeneous vehicle and a clear film, they speculated on the polymerization mechanism. With conjugated oils they suggested that a true copolymerization occurred by propagation across the unsaturated system, either 1, 2, or 1, 4.

Unconjugated oils were believed to be chain modifiers by a hydrogen-transfer process. In this transfer the catalyst or polymer radical abstracts a hydrogen atom from a methylene group *alpha* to a double bond, probably at the C_{11} position in an unconjugated 9,12-system. The methylene radical can initiate branching polymer chains of the monomer, or it may resonate with the unsaturation to throw the system into conjugation. Hewitt and Armitage believed modification by hydrogen transfer to be less favored than direct reaction with conjugation. This latter accounted for the better compatibility in copolymers of conjugated oils.

The course of reaction with either unconjugated or conjugated oils results in polymer branches of the monomer on the oil molecule, promoting compatibility in the vehicle. But branched copolymer is not the only reaction product.

The labile hydrogen in the monomer/oil system, which can transfer so readily to produce branching on the oil, is also active in chain transfer with the polymerizing monomer. Thus, of the monomer which homopolymerizes (polymerizes to the total exclusion of oil), a large portion is found in the form of short chains caused by the transfer activity of labile hydrogen both on oil molecules and on such solvents as xylene or toluene. These short chains render the homopolymer more soluble in the copolymer system.

There is evidence for still another type of reaction between oil and monomer, the Diels-Alder adduct formation. This takes place independently of the catalyst and involves a six-membered ring formation between the monomer and a conjugated system in the oil. Most of the monomers used in modification of vegetable oils are probably capable of undergoing some Diels-Alder reaction at the temperatures usually attained.

Heat-bodying of certain oils also has been found to occur under the conditions of monomer modification, especially in the presence of peroxide catalyst. But evidence shows that this change in the oil itself is usually small and not of overwhelming importance in determining the properties of copolymer vegetable oils.

In the 10 years from 1945 to 1955 there was much discussion of the true nature of copolymer oil chemistry. But in 1955 Crofts (5) again reached conclusions compatible with the course of reaction described above.

Three controllable process-variables also affect the course of the reaction between monomer and vegetable oil. It is important that the peroxide catalyst be one which decomposes at an optimum rate at the cooking temperature (Figure 4) (2). Furthermore the catalyst must be present at the proper concentration throughout the reaction. To this end it is becoming common to add the peroxide to the monomer first, thus assuring that a portion of the peroxide enters the reaction with each increment of monomer.

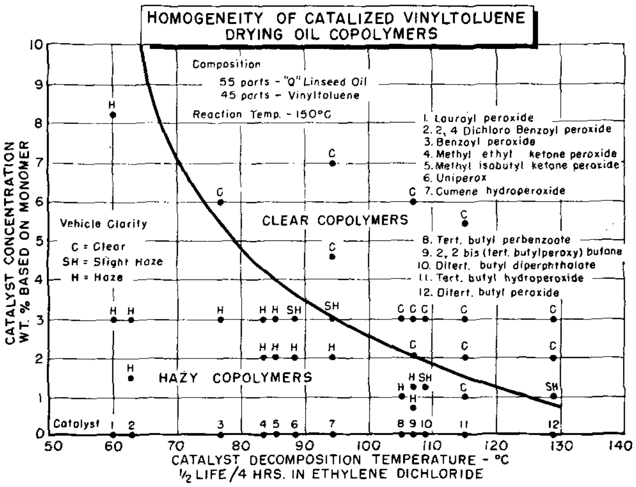

Fig. 4. Homogeneity of catalyzed vinyltoluene drying oil copolymers.

The type and quantity of solvent also affects the character of the polymerization. Large quantities of aromatic solvents such as xylene or toluene, with very active transfer of hydrogen on the methyl side chains, promote low-molecular-weight homopolymer and probably more efficient initiation of side branches of polymer on oil.

Higher temperature also promotes compatibility by aiding in the rapid formation of active centers, both by primary radicals and by hydrogen transfer. The formation of a high concentration of active centers reduces the average molecular weight of polymers and promotes mutual solubility.

There are a number of other unanswered questions about the chemistry of reaction between monomer and vegetable oil, but the complex products which result largely obscure the exact course and make it very difficult to detect changes in the product resulting from subtle differences in monomer, oil, or process conditions. As a sample "unanswered question," consider the reaction of vinyltoluene and coconut oil. Coconut oil is essentially saturated, yet the monomer modification takes place readily to produce a clear vehicle, and peroxides do promote this compatibility. Are mere traces of unsaturation in the coconut oil responsible for monomer branching, which brings about compatibility? Is the hydrogen on the carbon atom *alpha* to the carbonyl group of the oil sufficiently active to undergo transfer and branching of polymer on the oil? Is an actual covalent bond between polymer and oil even necessary to achieve compatibility?

Copolymer vegetable oils are interesting, both chemically and from the viewpoint of practical application. It would be satisfying to say that they were enjoying wide market acceptance, but such is not the case. They are well regarded in certain specialty gloss coatings for paper and in surface-conditioning primers for masonry; they have potential in interior gloss and semi-gloss enamels. Some of the monomer modified oils are reacted further to make monomer modified alkyds though the more common method of achieving this end is to prepare the oil/alkyd first, then to modify with vinyl monomer.

However if we broaden our definition to include monomer-modified alkyds, the market becomes truly significant. Copolymer vegetable oils themselves enjoy a market of perhaps 1 to 1.5 million pounds per year, of which roughly one-half is monomer. In addition, there are about 40 million pounds of monomer-modified alkyds prepared each year, with the monomer portion about one-third, or 15 million pounds.

REFERENCES

1. Buege, F. J., Cipriano, A. L., and Drubel, R. B., Offic. Dig. Federation Paint and Varnish Production Clubs, *27*, No. 362, 148–162 (1955).
2. Buege, F. J., Ind. Eng. Chem., *46*, 1695–1700 (1954).
3. Vranish, S. R., Jackman, R. M., Helmreich, R. F., and Henson, W. A., Offic. Dig. Federation Paint and Varnish Production Clubs, *29*, No. 384, 56 (1957).
4. Hewitt, D. H., and Armitage, F., J. Oil and Colour Chemists' Assoc., *29*, No. 312, 109 (1946).
5. Crofts, J. B., J. Appli. Chem. (London), *5*, 88 (1955).