11.59. The solvents used in the determinations were spectrograde methanol, chloroform, and iso-octane, and it was established that E max. did not vary with the solvents by determining the absorbance of a sample of $DNPE_1$ in each. The calculated E max. values from these determinations were all $1.90 \pm 0.02 \times 10^3$.

Discussion of Results

The plot of mole fraction *vs.* average molecular weight from countercurrent extraction of $DNPE_{9.15}$ (Figure 3) was made, using only the material which had a wavelength of maximum absorption of 276 mμ. This portion is represented by the broad middle peak in Figure 2 and amounts to 93.2% of the material charged to the Craig apparatus. Impurities, such as polyethylene glycol, polyolefins, alkylphenyl-alkyl ethers, etc., are apparently concentrated in the two small peaks 1 and 3. Mole fraction values in Figure 3 therefore represent mole fraction of only 93.2% of the total material (100% of the middle peak, which consists of ethylene oxide adducts of DNP). The displacement of the experimental curve from the calculated molecular-weight values might be partially attributed to this factor, but the distortion of the experimental curve and its wider molecular-weight distribution could readily result from failure of dinonylphenol to be completely converted to dinonylphenoxyethanol before "chaining" occurs.

Evidence for such an explanation is provided by the chromatography of $DNPE_{1.03}$ (Figure 1). Separation and identification of the chromatographed fractions established that this material contains approximately 15% of unreacted dinonylphenol, 61% of dinonylphenoxyethanol, and 18% of oxyethylated dinonylphenol with more than one oxyethylene unit, which analyses indicated is principally $DNPE_2$ with smaller amounts of higher analogs. It was ascertained that the unreacted dinonylphenol fraction (Peak No. 1) consists principally of unreacted 2,4-dinonylphenol by infrared examination and by other oxyethylation experiments wherein more than one mole of ethylene oxide was added to 1 mole of dinonylphenol. The product from the addition of 2 moles of ethylene oxide to 1 mole of dinonylphenol was chromatographed by a similar procedure and found to contain only about 3% of material not oxyethylated. The infrared spectrum of the material in Peak No. 1 from the chromatography of $DNPE_{1.03}$ showed absorption (830 $cm.^{-1}$ and 885 $cm.^{-1}$) characteristic of 1,2,4-trisubstitution and the absence of absorption (770 $cm.^{-1}$ and 790 $cm.^{-1}$) characteristic of 1,2,3-trisubstitution, thus indicating a 2,6-dialkylphenol concentration of less than 5% in Peak No. 1.

Steric factors offer a likely explanation for the difference between dinonylphenol oxyethylations and oxyethylations of phenol and p-alkylphenols, which proceed by nearly quantitative conversion of the phenol to the phenoxyethanol before appreciable "chaining" occurs. Molecular models indicate that the presence of a bulky alkyl group ortho to the phenolic hydroxy group could hinder formation of the phenoxyethanol while not interfering with the normal "chaining" process after the chain length is sufficient to remove the site of reaction beyond the influence of the ortho alkyl group.

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Fatty Acid Morpholides as Plasticizers for Vinyl Chloride Resins. II. The Morpholides of Selectively Hydrogenated and of Epoxidized Cottonseed Fatty Acids[1]

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The morpholides of selectively hydrogenated cottonseed acids and of epoxidized cottonseed acids have been prepared and shown to be good primary plasticizers for vinyl chloride homopolymer and copolymer resins. They are also acceptable plasticizers for cellulose triacetate and possibly also as Buna A softeners. The degree of hydrogenation or partial epoxidation was approximately that equivalent to the conversion of all the polyunsaturated acyls to monounsaturated acyls.

As PREVIOUSLY REPORTED from this laboratory, the mixed morpholides prepared from composite cottonseed oil fatty acids exhibit good plasticizing properties in vinyl resins except for poor compatibility (1). This incompatibility was attributed to the presence of saturated and polyunsaturated morpholides in the mixture since the morpholides of stearic, palmitic, and linoleic acids are all incompatible. A process for preparing a compatible morpholide mixture from cottonseed acids was developed which involved removal of the major portion of the satu-

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rated acids and reduction in the proportion of polyunsaturation in the resulting unsaturated fraction by selective hydrogenation or by partial epoxidation (1,2,3).

Experiments with binary mixtures of the morpholide of oleic acid with the morpholides of stearic and palmitic acids showed that much larger proportions of the palmitic than of the stearic acid morpholide can be tolerated without causing incompatibility (4). This led to the conclusion, now confirmed by the results of the present communication, that, since palmitic acid is the only major saturated constituent in cottonseed fatty acids, a compatible morpholide mixture could be made from the composite acids by selective hydrogenation or by partial epoxidation without removing the saturates.

Experimental

Hydrogenated cottonseed acids, mainly palmitic and monounsaturated acids, were obtained by saponifying a refined cottonseed oil (iodine value, 108.8; thiocyanogen value, 69.9) which had been selectively hydrogenated to an iodine value of 63.1 and a thiocyanogen value of 62.9. The hydrogenation was performed under conditions—hydrogen pressure 2–3 p.s.i.g.; 400°F.; 0.5% nickel catalyst—which converted substantially all the linoleoyl to oleoyl and precluded the formation of appreciable amounts of the stearoyl moiety.

The morpholide of these acids was prepared by the general procedure previously described (1). However certain modifications were introduced to increase the over-all yields and reduce the residual free fatty acids in the final product.

The use of 5% of benzene (exclusive of the capacity of the Dean-Stark trap) and a 50% excess of morpholine in the reaction mixture resulted in a 64% conversion of the acids to the morpholides in 4 hrs., 90% in 6 hrs., and 96% in 8 hrs. Longer periods of refluxing caused an enhancement in color. The use of 7.5% (of the reaction mixture) of Amberlite IRA-400 resin as a catalyst (5) gave an 88% conversion after 4 hrs. but only 90% after 6 hrs. of refluxing.

The removal of unreacted fatty acid from the morpholides was effected either by percolation through an activated alumina column or by slurrying with Amberlite IRA-400 resin in free-base form. A column, 2.5 cm. in diameter x 25 cm., containing 172 g. of Alorco F-1 Grade, 14–28 mesh alumina, reduced the acidity of 85 g. of morpholide from 9%, expressed as oleic acid, to an untitratable value. To improve the percolation rate 1 part of the morpholide was diluted with 2 parts of either cyclohexane or commercial hexane.

One part of Amberlite resin was vigorously slurried for 20 min. with 2 parts of the same crude morpholide. The acidity of the morpholide, after filtering off the spent resin, was 0.29%. Percolation through a column of resin proved to be less efficient than slurrying.

Under carefully-controlled reaction conditions the product is a deep yellow, 5–6 on the Gardner scale. Darker products, as high as 17–18 on the Gardner scale, are sometimes obtained when either the starting materials are highly colored or the reaction period is unduly prolonged. Some color improvement in the product is achieved by the alumina deacidification treatment. Distillation at reduced pressure (2–3 mm.) results in color upgrading to 1–2 on the Gardner scale. The distilled product had a density of 0.930 g./ml. and a viscosity of 46.5 centipoises at 25°C.

The epoxidized cottonseed fatty acid morpholide (iodine value, 40.1; oxirane oxygen content, 2.62%; density, 0.966 g./ml., and viscosity, 70.2 centipoises at 25°C.) was prepared by perbenzoic acid epoxidation of the morpholide (iodine value, 90.8; thiocyanogen value, 58.3) of the composite fatty acids obtained from the original refined cottonseed oil. This degree of epoxidation was approximately equivalent to that required to convert all the linoleoylmorpholine in the original mixture to epoxy-oleoylmorpholine.

The morpholide samples were screened as plasticizers for 95% poly(vinyl chloride)–5% poly(vinyl acetate) copolymer (Vinylite VYDR) and for poly(vinyl chloride) (Geon 101). The compounding formulation used was as follows: resin (Vinylite VYDR or Geon 101), 63.5%; plasticizer, 35.0%; stearic acid, 0.5%; basic lead carbonate, 1.0%. When more or less than 35% of plasticizer was used, the resin content was varied in accordance with the formula: % of resin = (98.5 − x), where x is the percentage of plasticizer. The milling, molding and testing procedures followed those previously reported (1,6), but 12- to 16-mil instead of 76-mil sheets were used for the volatility

TABLE I

Physical Properties of Vinyl Chloride Polymer and Copolymer Resins Plasticized with Morpholides of Acids from Cottonseed Oil

Sample	Morpholide of	Plasticizer	Tensile strength	100% modulus	Elongation	Brittle point	Volatility loss	Compatibility [a]
Poly(vinyl chloride–vinyl acetate) copolymer		%	p.s.i.	p.s.i.	%	°C.	%	
1	Cottonseed acids [b]	35	2660	1200	330	−45	......	I
2	Epoxidized cottonseed acids	35	2940	1210	400	−26	0.73	C
3	Hydrogenated cottonseed acids	25	3800	2710	290	−31	0.90	C
4	Hydrogenated cottonseed acids	30	3280	1830	340	−37	0.98	C
5	Hydrogenated cottonseed acids	35	2910	1390	360	−43	1.26	C
6	Hydrogenated cottonseed acids	40	........[c]	980	......[c]	−45	1.11	C
7	DOP (control)	25	3890	3210	300	−27	1.69	C
8	DOP (control)	30	3390	2290	300	−27	1.86	C
9	DOP (control)	35	3050	1690	330	−33	1.99	C
10	DOP (control)	40	2390	1120	350	−37	2.36	C
Poly(vinyl chloride)								
11	Cottonseed acids [b]	35	3090	1580	310	−43	......	I
12	Hydrogenated cottonseed acids	25	3930	2820	280	−25	1.09	C
13	Hydrogenated cottonseed acids	30	3380	2190	290	−35	1.21	C
14	Hydrogenated cottonseed acids	35	2910	1500	330	−37	1.01	C
15	Hydrogenated cottonseed acids	40	........[c]	1080	......[c]	−39	1.53	C
16	DOP (control)	25	3940	3390	280	−17	1.73	C
17	DOP (control)	30	3500	2380	330	−23	2.00	C
18	DOP (control)	35	3170	1750	320	−33	2.20	C
19	DOP (control)	40	2520	1200	330	−37	2.33	C

[a] C = compatible; I = incompatible.

[b] Reference (1).

[c] Sample elongated, without rupture, beyond range of IP-4 tester.

tests. Compositions containing 25 and 30% plasticizer were milled and molded at 340°F., and those containing 35 and 40% at 310°F. Compositions which showed no signs of bleeding or smearing during a shelf-aging of 90 days were classified as compatible.

Cellulose acetate-morpholide compositions were prepared and tested for compatibility as previously described (7). A compatible composition was one which showed no signs of bleeding, spontaneous opacity, or opacity induced by creasing and could be repeatedly flexed without cracking.

The evaluations of these materials as Buna N (Hycar 1042—33% acrylonitrile) softeners were conducted by standard procedures (8).

Results and Discussion

The results for the plasticizer evaluation in Vinylite VYDR and Geon 101 resins are summarized in Table I. The data for the morpholide of unmodified cottonseed fatty acids (Samples 1 and 11) are included for comparison.

These morpholide plasticizers are all more efficient than the control, di-2-ethylhexylphthalate (DOP), at the same compositional level. The morpholide-plasticized copolymer and homopolymer stocks are superior to the control in 100% modulus, volatility, and except for the epoxidized sample, in low-temperature characteristics. The hydrogenated cottonseed morpholides offer a low-temperature performance, approaching that of the adipates without the highly unfavorable volatilities of the latter. All morpholide stocks are more or less comparable to the control in tensile strength and elongation. Their plasticizing performance is somewhat better in copolymer than in homopolymer compositions, thus paralleling the performance of DOP.

The incompatibility of the morpholides of the unmodified cottonseed acids (Samples 1 and 11) is thus overcome by partial epoxidation or selective hydrogenation of the polyunsaturated acyls to monounsaturated acyls (Samples 2,5, and 14). A compatibility equal to that of DOP is achieved in the hydrogenated samples, based on a 12-month test period, without any sacrifice in plasticizer performance. Epoxidation results in a moderate sacrifice in low-temperature performance but is advantageous in that it confers markedly improved long-range thermal stability to the plastic composition. Under identical accelerated test conditions such compositions retained more than 50% of their original reflectance while the unepoxidized morpholide compositions (Samples 5 and 14) and the control (Sample 9) failed completely.

Morpholides of the long-chain saturated fatty acids up to palmitic have already been recognized as plasticizers for cellulose triacetate (9). It now appears that this utility extends to certain mixtures of fatty acids beyond the 16-carbon chain length. The morpholides of oleic, linoleic, composite cottonseed, hydrogenated cottonseed, and epoxidized cottonseed acids were all found to be compatible plasticizers for cellulose acetate (41% acetyl) at concentrations of 20 parts of plasticizer to 100 parts of resin. At concentrations of 30 parts of plasticizer to 100 parts of resin however only the morpholides of the hydrogenated and epoxidized cottonseed acids were compatible.

A few tests were performed to determine the behavior of these morpholides as Buna N softeners. Comparative observations were made on Buna N stock softened with 10.2% dibutyl sebacate (control) and 10.2% of the hydrogenated cottonseed morpholide. Whether aged or unaged, the morpholide stock was equivalent and, in most instances, superior to the control in tensile strength, 300% modulus, elongation, and volatility. The control stock, on the other hand, has a superior brittle point, −50°C. as against −40°C., and also exhibits a smaller volume change (less swelling) after steeping in the test solvent mixture. Although a slight exudation was detected in the morpholide composition after 30 days, this did not increase during the next 90 days.

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