continuous arrangement the Votator pump can possibly be used to push the material through the whole system.

An air-operated diaphragm-pump was used for our tests; air pressure at the beginning of filtration was 10 p.s.i., which was slowly increased to about 15 p.s.i. with the formation of a layer of crystals in the filter.

Separation. Separation of the liquid portion from the crystallized portion was achieved by centrifugal means or with filters. A regular plate and frame filter, covered with duck filter-cloth and No. 230 filter-paper, performs sufficiently well, in particular after a crystal layer has been built up on the filter paper. The crystallized material gets an additional hold-up time in the filter-press, and an increase in cold test was noted. In addition, the high concentration of crystals in the press probably not only filters the oil mechanically but also causes a final crystallization of high-melting glycerides.

The flow rate of this system was adjusted in such a way that the oil in-flow from the Votator chilling unit was equal to the pumping rate through the filter, and the crystallization pails had a capacity of about 3 hrs. of oil flow. Tests were run continuously for about 8 hrs. each and gave good and reproducible results. One example of a series of samples is listed in Table IV.

Yields of salad oil were in the order of 75–78% of the incoming oil. A baffle system was tried as a truly continuous hold-up arrangement, but by-passing occurred and the salad oil had a cold test in the order of only 15 hrs. Centrifugal separation of the liquid and solid phases was investigated because it would be a further step towards continuous operation.

A laboratory Sharples Super-Centrifuge was tried with both the separating bowl (discharge of two streams) and the clarifying bowl (solid fraction remaining behind). Only the clarifying bowl gave good results. The crystallized material after a 3½–4-hr. hold-up time was separated with a centrifugal force of about 6,500 x g. The liquid discharge was perfectly clear, and the salad oil had a cold test of 16–20 hrs., with an average yield of 80%.

A basket type of laboratory centrifuge produced only an unsatisfactory separation with centrifugal forces of up to 1,800 x g, both with a solid bowl and with a perforated bowl lined with filter-cloth and filter-paper. A schematic outline of the whole process can be seen in Figure 2.

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The Oxyethylation of Dinonylphenol

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Countercurrent extraction data have shown that ethylene oxide adducts of dinonylphenol have a wider molecular-weight distribution than is predicted by the Flory-Poisson calculation. The difference is attributed to the fact that the dinonylphenol is not completely converted to dinonylphenoxyethanol before subsequent monomer additions occur.

THE USE of 4-alkyl and 2,4-dialkylphenols as substrates in the preparation of nonionic surface-active materials by the base-catalyzed reaction with ethylene oxide is well known (1,2). Flory (3) has described a method of calculation of the molecular-weight distribution of polymers obtained by oxyethylation reactions and has shown that a Poisson (4) distribution will be obtained in such reactions, provided that the number of propagating units remains constant and that the polymer chains are built up by a sequence of kinetically identical additions of monomer. Weibull and Nycander (5) have demonstrated that the oxyethylation of ethylene glycol meets the requirements of the Flory calculation and results in polymers having a Poisson distribution. Miller, Bann, and Thrower (6) observed that in base-catalyzed oxyethylations of phenol, the phenol is first exclusively converted to phenoxyethanol before any subsequent monomer additions ("chaining") occur and that a Poisson type of distribution results from the subsequent addition of ethylene oxide. Similar results were obtained by Mayhew and Hyatt (7) from oxyethylations of p-nonylphenol and by Kelly and Greenwald (8) from a study of the molecular-weight distribution of oxyethylated p-t-octylphenol. Therefore the molecular-weight distribution of oxyethylated phenol and p-alkylphenols apparently can be calculated by the method of Flory, considering the phenoxyethanols as the propagating units.

Countercurrent extraction data obtained in these laboratories have indicated that oxyethylated dinonylphenol has a molecular-weight distribution not in agreement with the Poisson distribution, calculated by the method of Flory. The disagreement may result because one of the basic conditions required for adaptation of the Flory calculation to phenols (*i.e.*, that all of the phenol is first converted to the phenoxyethanol before "chaining" occurs) fails to apply to dinonylphenol oxyethylations. This fact was substantiated by chromatographic data which have demonstrated that appreciable "chaining" does occur in dinonylphenol oxyethylations before all the dinonylphenol has been converted to dinonylphenoxyethanol. As a result of this premature "chaining" dinonylphenol-ethylene oxide polymers have a wider molecular-weight distribution than would be expected on the basis of calculation by the method of Flory.

Experimental

Preparation of Dinonylphenol. Dinonylphenol (DNP) was synthesized by the boron trifluoride-catalyzed reaction of propylene trimer (a complex

mixture of olefins averaging C_9 and obtained from Sun Oil Company) with U.S.P. phenol. The crude product was distilled through a 10-plate Oldershaw column, and DNP, b.r. 207–225°C./10 mm., was obtained. Hydroxyl number: found, 156; theory, 162.

Oxyethylation of Dinonylphenol. Conventional base-catalyzed oxyethylation procedures (2) were used to add ethylene oxide to dinonylphenol. Adducts prepared by using 1.03 moles ethylene oxide/ mole DNP ($DNPE_{1.03}$) and 9.15 moles ethylene oxide/mole DNP ($DNPE_{9.15}$), respectively, were employed in the chromatographic and countercurrent extraction studies.

Chromatography of $DNPE_{1.03}$

Materials

Silicic acid: Mallinckrodt Analytical Reagent, 100 mesh

Benzene: Baker and Adamson A.C.S. Reagent Grade

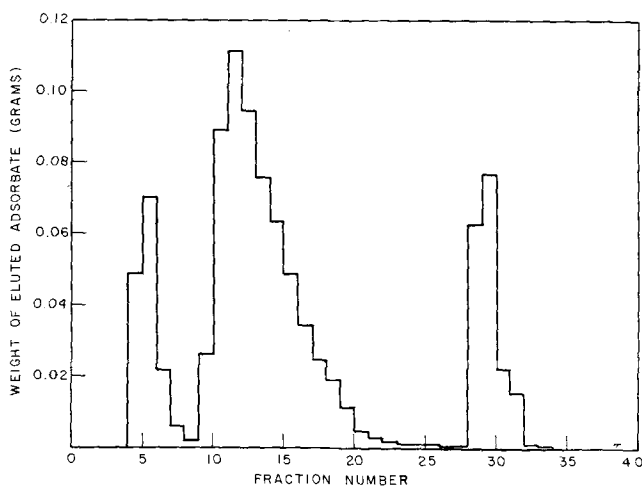Aluminum oxide: Merck Reagent "suitable for chromatographic adsorption"

FIG. 1. Silicic acid chromatogram of $DNPE_{1.03}$. Eluant schedule: benzene (fractions 1–27); acetone (fractions 28–38).

Acetone: Baker and Adamson A.C.S. Reagent Grade

Procedure

A 53 x 2-cm. column was packed, using a slurry of 45 g. of silicic acid in benzene which had been prepurified by passing through a column of aluminum oxide. Glass wool and Ottawa sand were used at the top and bottom of the column for protection of the surface from mechanical disturbances. The $DNPE_{1.03}$ (1.0000 g.) was charged as a solution in 5–10 ml. of benzene. The separation was run under a pressure of about 25 cm. of dried, purified nitrogen applied at the top of the column via a ball-joint connection. Measured volume fractions (13.5 ml.) were collected and evaporated free of solvent in a stream of dry,

Peak No.	Wt. adsorbate g.	% C		% H	
		Found	Calc.	Found	Calc.
1	0.1485	82.94	83.17[a]	12.33	12.22[a]
2	0.6141	79.86	79.94[b]	11.79	11.87[b]
3	0.1808	76.66	77.36[c]	11.55	11.59[c]
Total	0.9434				

[a] Theory for DNP ($C_{24}H_{42}O$).
[b] Theory for $DNPE_1$ ($C_{26}H_{46}O_2$).
[c] Theory for $DNPE_2$ ($C_{28}H_{50}O_3$). Theory for $DNPE_3$ ($C_{30}H_{54}O_4$) is C, 75.26; H, 11.37.
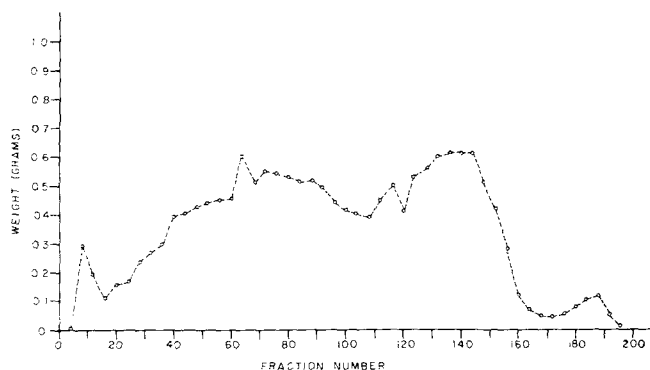
FIG. 2. Weight distribution of $DNPE_{9.15}$ from a 200-transfer countercurrent extraction with a chloroform, methanol, iso-octane, water (10:35:50:5) system.

filtered nitrogen. The eluted adsorbate was weighed, and the weight was plotted vs. the volume of eluate (Figure 1). The solvent schedule was: benzene (for peaks 1 and 2); acetone, prepurified over aluminum oxide (for peak 3).

Results

Countercurrent Extraction of $DNPE_{9.15}$. Countercurrent extractions were carried out on the sample of $DNPE_{9.15}$ in a Craig apparatus to effect 200 transfers, using a chloroform, methanol, iso-octane, water (10:35:50:5) system. Aliquots of both top and bottom layers were taken from every fourth tube, and the solvent was evaporated to follow the weight and partition coefficient distribution of the sample. The countercurrent weight data showed a small peak in the beginning tubes No. 0–16, a large broad peak spreading from tube No. 17 to tube No. 172, and a third distinct peak including the remaining tubes to No. 199 (Figure 2). The molecular-weight distribution of the polymer (Figure 3) was followed spectroscopically by using a Beckman DK-2 spectrophotometer. The wavelength of maximum absorbance was at 276 mμ except for the material (approx. 7 wt. %) in the beginning and end cuts, which occurred in the small peaks 1 and 3 in Figure 2. The value of 1.90 x 10^3 was used for E max. on the basis of results obtained from spectroscopic analysis of chromatographically purified samples of $DNPE_1$ and $DNPE_2$, with known molecular weight, by the same procedure. The pure $DNPE_2$ was obtained by the chromatographic procedure described previously, using a 1:1 chloroform-benzene solvent to separate the $DNPE_2$ from $DNPE_3$ and higher members. For $DNPE_2$ % C: Fd., 77.29; Calc., 77.36. % H: Fd., 11.93; Calc.,
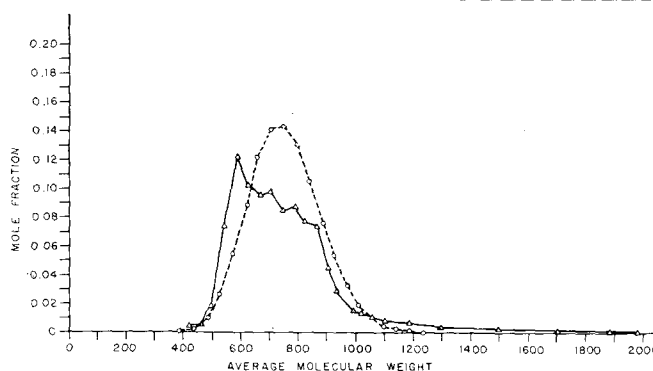
FIG. 3. Molecular-weight distribution of $DNPE_{9.15}$.
△—Experimental
○—Calculated by method of Flory (3)

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 DNPE₁ 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 dinonyl-phenoxyethanol 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.

Acknowledgment

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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-