

tivities of the 9, 12, and 15 double bonds. Comparing Run 26 with Run 25 in Table III, it can be shown that the absorption of 73% as much hydrogen caused the disappearance of only 54% as much linolenic acid. The only difference in the conditions of these two runs was in the amount of catalyst. It is concluded that a higher Rufert nickel catalyst concentration favors hydrogenation of linolenic acid in preference to less unsaturated acids.

### Acknowledgment

The authors wish to express their appreciation to H.M. Teeter of the Northern Utilization Research and Development Division, Peoria, Ill., for his assistance in supervising this study.

### REFERENCES

1. Bailey, A.E., *J. Am. Oil Chemists' Soc.*, **26**, 644-648 (1949).
2. Bailey, A.E., and Fisher, G.S., *Oil and Soap*, **23**, 14-18 (1946).
3. Bauer and Ermann, *Chem. Umschau*, **37**, 241 (1930).

4. Beadle, B.W., *Oil and Soap*, **23**, 140-145 (1946).
5. Begemann, P.H., Keppler, J.G., and Boekenooogen, H.A., *Rec. Trav. Chim.*, **69**, 439-456 (1950).
6. Boelhouwer, C., Gerckens, J., Lie, Ong Tian, and Waterman, H.I., *J. Am. Oil Chemists' Soc.*, **30**, 59-61 (1953).
7. Feuge, R.O., Cousins, E.R., Fore, S.P., Du Pre, E.F., and O'Connor, R.T., *J. Am. Oil Chemists' Soc.*, **30**, 454-460 (1953).
8. Frampton, V.L., Edwards, J.D., and Henze, H.R., *J. Am. Chem. Soc.*, **73**, 4432-4434 (1951).
9. Hilditch and Vidyarthi, *Proc. Roy. Soc. (London)*, **122A**, 563 (1929).
10. Jones, E.P., and Stolp, J.A., *J. Am. Oil Chemists' Soc.*, **35**, 71-76 (1958).
11. Lemieux, R.U., and von Rudloff, E., *Can. J. Chem.*, **33**, 1701-1709 (1955).
12. Lemon, H.W., *Can. J. Res.*, **22F**, 191 (1944).
13. Lemon, H.W., *Can. J. Res.*, **25F**, 34 (1947).
14. Lindlar, von H., *Helv. Chim. Acta.*, **35**, 446-450 (1952).
15. McCutchan, J.W., *Org. Syntheses, Collective Vol. 3*, 531 (1955).
16. Mitchell, J.H. Jr., Kraybill, H.R., and Zscheile, F.P., *Ind. Eng. Chem.*, **15**, 1-3 (1943).
17. Official and Tentative Methods of the American Oil Chemists' Society, Tentative Method Cd 7-48.
18. Rebello, D., and Daubert, B.F., *J. Am. Oil Chemists' Soc.*, **28**, 177-182 (1951).
19. Rebello, D., and Daubert, B.F., *J. Am. Oil Chemists' Soc.*, **28**, 183-185 (1951).
20. van der Veen, H., *Chem. Umschau, Felte, Oels, Wachse und Harzze*, **58**, 89 (1931).

[Received November 18, 1959]

## The Production of Salad Oil by Fractional Crystallization With Solvents

W.G. MERTENS, L.J. RUBIN, and B.F. TEASDALE, *Canada Packers Ltd., Toronto, Canada*

A fractional crystallization method for the winterization of cottonseed oil with solvents was developed in our laboratories and pilot plant.

Small amounts of solvent (*e.g.*, 10% by weight of acetone) were mixed with the oil. This mixture was rapidly chilled to 0°C. and kept at this temperature for 3-4 hrs.; the liquid portion was separated from the solids.

After solvent evaporation a salad oil of good quality was obtained. The yield is equal to or better than that obtained with conventional methods.

The method is suitable for a continuous operation since rapid chilling can be used, and only a short over-all time is necessary. Great advantages of the process are the use of low amounts of solvent and of a refrigeration system not requiring temperatures below 0°C.

**T**HE HIGHER-MELTING GLYCERIDES in cottonseed oil crystallize out at refrigerator temperature and therefore have to be removed in order to obtain a salad oil. This is usually done by the well-known winterization process, in which the oil is slowly cooled to facilitate a partial crystallization, and the crystallized portion is separated from the liquid oil by filtration.

With this conventional winterization method it is difficult to obtain good-sized, easily-filterable crystals, and the rate of cooling as well as the rate of filtering is quite slow. "Because of the slowness of the operation and the poor separation obtained, ordinary winterization is one of the least satisfactory of present oil-processing methods" (1).

Efforts have been made by many workers to improve this conventional method, and the most promising ways seem to be the use of crystal modifiers (13) and solvents.

The great advantage of using a solvent-oil mixture for fractional crystallization lies in the fact that "equilibrium between the solid and liquid phases is

established much more rapidly, large easily-separable crystals are produced even at relatively-high cooling rates, and the viscosity of the liquid phase is reduced so that separation of the crystals by filtration or other means is more rapid" (1).

Previously-reported solvent crystallization methods employ large amounts of solvents (the average oil: solvent ratio is 1:3) at relatively low temperatures (from -3° to -60°C.). Methods have been developed for a variety of fatty substances (*e.g.*, fatty acids, lard, tallow), including peanut oil and cottonseed oil (2,3,4,5,6,14).

The solvent winterization method developed in our laboratories is different from previously described methods in that it uses very small amounts of solvent (in the order of 10%). The small amount of solvent is a major advantage of this method since it eliminates the need for large-scale solvent handling equipment and reduces solvent losses markedly. A wide variety of solvents was found to be useful.

Even with this small amount of solvent however, a fast chilling of the oil-solvent mixture in a Votator type of heat exchanger is possible, and the temperature desired for further crystallization (around 0°C.) can easily be maintained with regular refrigeration equipment. Contrary to our expectation, these conditions do not result in the formation of an unmanageable gel but produce large-sized, easily-filterable crystals. The necessary crystallization time at about 0°C. is only 3-4 hrs. as compared with 1-2 days for regular winterization. This eliminates the need for large-capacity refrigerated tanks and opens the way for a continuous winterization process.

One commercially-used continuous solvent winterization method (6,7) usually employs 50-60% hexane. It takes advantage of the fact that the oil is already

in a solvent solution (miscella) after solvent extraction and solvent refining. Our method is intended for the oil processor who starts his winterization process with refined cottonseed oil. In this case it would seem to be of great economic advantage to use as small an amount of solvent as possible and relatively small hold-up facilities, yet to be able to employ a fast chilling step.

Under the conditions of our method a yield of 75-78% cottonseed salad oil with a cold test of 15-20 hrs. was obtained. Longer holding times (6-8 hrs.) gave longer cold tests (up to 60 hrs.).

This solvent winterization method combines the advantages of a low temperature, large solvent amount crystallization (fast crystallization without solidification of the mass) with the economic advantages of regular refrigeration temperatures and low solvent losses because of the small amounts of solvents used.

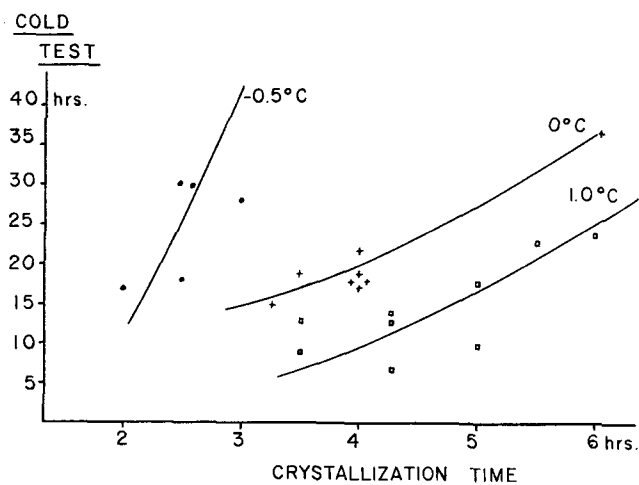


FIG. 1. Increase in cold test with increasing crystallization time. Solvent:10% acetone.

Previous publications (3,4,5,14) give the general impression that low-temperature crystallization of cottonseed oil with solvent amounts smaller than about 25% of the weight of the oil would lead to the crystallization of large amounts of high-melting glycerides and would produce a material of high viscosity, possibly a gel, which cannot be separated into solid and liquid fractions.

Since it was realized that great economic advantages were possible if one could increase the temperature above the -10 to -15°C. range commonly used, at the same time reduce the amount of solvent as much as possible and still get a good crystallization in a reasonably short time, tests were started in our laboratories to investigate these points.

**Experimental**

**1. Laboratory Tests**

Different amounts of acetone were mixed with cottonseed oil and stored at 0°C. We were able to reduce the solvent amount to 10% without causing the oil-solvent mixture to crystallize excessively during a time of 3-4 hrs. Solid and liquid phases could be separated easily, and the winterized salad oil obtained had a cold test of 15-20 hrs.

*Standard Procedure.* First, 90 g. of refined, bleached cottonseed oil were mixed with 10 g. of acetone in an

TABLE I  
Cold Test of Cottonseed Oil, Solvent-Winterized with Different Solvents

Solvent	Crystallization temperature: 0°C.						
	Ace.	MEK.	MIK.	MAc.	EAc.	IPA.	EEt.
Solvent concentration: 10%							
Cr. time:							
4 hrs. ....	22	20	9	3	8	4	8
6 hrs. ....	40	38	38	35	30	27	27

Erlenmeyer flask and stored in a bath of melting ice. The flask was stirred gently during the first 10 min. to obtain a fast chilling, and the mixture was then allowed to crystallize without agitation at 0°C. Samples were taken at regular intervals and filtered in the cooler through Reeve Angel No. 230 filter paper; the solvent was evaporated on a hotplate under a stream of nitrogen. Cold tests and I.V. were determined. An example is given in Figure 1.

The standard conditions, which are outlined above, were varied in order to find optimum operating conditions and tolerance levels.

*Different Solvents.* Various solvents are mentioned in the literature for solvent crystallization of fatty material (5,6,8,10). Many of these proved to be useful for our method. Satisfactory results were obtained with 10% of acetone, methyl ethyl ketone, methyl isobutyl ketone, ethyl acetate, isopropyl acetate, and ethyl ether. Good results were also obtained with 20% of dimethyl formamide.

These solvents help to form large, easily-filterable crystals and allow (or assist) the high-melting portion of the oil to crystallize out. They have the ability to prevent the oil from turning into a stiff, gelatinous mass under the test conditions and thereby make this fast process possible. There is a tendency toward the formation of a gel with increasing molecular weight of the members of a solvent group.

Some test results with different solvents are listed in Table I.

Unsatisfactory solvents under the test conditions (0°C., 10% solvent) were the higher alcohols, chlorinated hydrocarbons, hexane, petroleum ether, benzene, toluene, and tetrahydrofuran. Either a stiff, gelatinous mass was formed (alcohols, carbon tetrachloride, perchloroethylene), or crystallization was too slow and therefore did not produce an adequate cold test (benzene, toluene, hexane). It must be understood however that a lower crystallization temperature would make it possible to use solvents which exhibit a slow rate of crystallization at 0°C.

*Temperature Changes and Solvent Concentration.* The crystallization rate depends upon the relation of temperature to amount of solvent. A lower tempera-

TABLE II  
Solvent Crystallization of Cottonseed Oil at -2.2 and -4.0°C.  
Solvent concentration: 15%

Solvent	Crystallization time	Salad oil cold test
	hrs.	hrs.
Temp. -2.2°C.		
Acetone.....	2.5	8.5
M.E. Ketone.....	2.5	10.5
M. Ib. Ketone.....	2.5	8.5
Met. Acetate.....	3.5	stiff mass
Et. Acetate.....	2.5	3.5
Ip. Acetate.....	2.5	3.5
But. Acetate.....	3.5	stiff mass
	2.5	stiff mass
Temp. -4.0°C.		
Acetone.....	2.0	stiff mass
M.E. Ketone.....	2.0	stiff mass
Et. Acetate.....	2.0	stiff mass

TABLE III

Solvent Crystallization of Cottonseed Oil with Moisture in the Solvents  
Solvent concentration: 10% I.V. of cottonseed oil: 107.5

Solvent	I.V. at a crystallization time of (hrs.)			Cold test at crystallization time of (hrs.)	
	3	4	6	4	6
Acetone dry.....	108.7	112.5	114.0	17	36
Acetone 2% water.....	110.1	112.8	114.3	23	27
Acetone 4% water.....	109.7	112.7	113.9	24	31
M.E.Ketone dry.....	109.2	114.3	114.1	25	38
M.E.K. water sat.....	108.9	114.1	114.2	21	44
M.Ib.Ketone dry.....	108.7	112.6	114.6	9	48
M.Ib.K. water sat.....	109.3	113.1	113.4	14	48
Ethyl acetate dry.....	108.7	111.7	114.1	8	25
E.A. water sat.....	108.6	112.4	113.7	9	27
Isop. acetate dry.....	108.4	110.1	113.8	4	41
Ip. A. water sat.....	107.8	111.4	114.1	5	25

ture will increase the crystallization rate and shorten the process, but it may also lead to the formation of an unfilterable gelatinous mass. This however can be prevented by the use of more solvent.

With our preferred solvent concentration of 10% a temperature of from  $-0.5^{\circ}$  to  $1.0^{\circ}\text{C}$ . has to be maintained during chilling and hold-up time if one wants to use the shortest possible crystallization time of about 3-4 hrs. This temperature is however not essential for the method as such, and slightly higher temperatures may be used. In order to obtain a salad oil of the same cold test, higher temperatures require longer holding times. Temperatures below  $-0.5^{\circ}\text{C}$ . require more than 10% solvent. A fair crystallization rate was obtained at  $-2.2^{\circ}\text{C}$ . with 15% of ketones and acetates, but even more solvent has to be used at  $-4^{\circ}\text{C}$ . (Table II).

The emphasis of our process is on the use of small amounts of solvent. We did not investigate the use of large solvent amounts at lower temperatures in order to shorten the crystallization time below the 3-4 hrs. required in our procedure.

The use of larger amounts of solvents, lower temperatures, seeding with crystals, or the use of special crystal modifiers are however suggested as possible ways to a shorter time-cycle. The use of crystal modifiers was not investigated; they might also make the use of other solvents at different concentrations, and at different temperatures, possible.

The gain in over-all time due to fast crystallization at the lower temperatures was not significant. If, on the other hand, the solvent amount at the regular temperature of  $0^{\circ}\text{C}$ . was increased from 10 to 20%, most solvents showed too slow a crystallization rate. Only dimethyl formamide gave a better performance at the higher (20%) concentration.

*Water in the Solvent.* It is reported that water in the solvent, condensed from the air or stemming from the oil, may influence the crystallization behavior (5,9,10).

Acetone with up to 4% water, and water-saturated methyl ethyl ketone (11.9%  $\text{H}_2\text{O}$ ), methyl isobutyl

ketone (1.7%  $\text{H}_2\text{O}$ ), ethyl acetate (2.8%  $\text{H}_2\text{O}$ ), and isopropyl acetate (2.3%  $\text{H}_2\text{O}$ ) were tested. No significant differences in the winterization behavior of these solvents as compared with dry solvents were found under the test conditions. A solvent with a low level of water saturation would allow the process to be run under very stable conditions since it could be used fully saturated and excess water would settle out (Table III).

*Crystallization Time.* An increase in the hold-up time during crystallization of the oil produces a salad oil with a higher cold test (Figure 1, Tables I and III). One has hereby an easy means of adjusting the final salad oil properties. A crystallization time of 3-4 hrs. (with 10% solvent at  $0^{\circ}\text{C}$ . and with slight agitation of the material) will give a salad oil with a 15-20-hr. cold test; 6 hrs. of crystallization time gave 30-40-hr. cold tests, and 6-8 hrs. of hold-up time produced salad oil with up to 60-hr. cold tests.

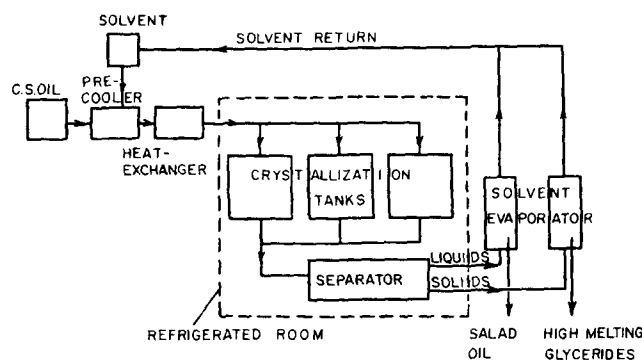


FIG. 2. Schematic outline of solvent winterization process.

*Agitation and Seeding.* The crystallization rate is speeded up by a slight agitation of the material. This helps to contact all oil portions with the first crystal nuclei and gives fast and uniform crystallization.

Seeding, the addition of 2% cottonseed oil press-cake to the oil-solvent mixture in the precooling stage at about  $10^{\circ}\text{C}$ ., increased the crystallization rate during the hold-up time too much and resulted in the formation of a stiff, gelatinous mass.

## 2. Pilot-Plant Tests

After the process conditions had been established by laboratory tests, work was transferred to the pilot plant. The following procedure was employed.

*Precooling.* Refined and bleached cottonseed oil was pre-cooled under agitation to about  $10^{\circ}\text{C}$ .

*Solvent Addition.* Ten percent by weight of acetone was added to the oil and mixed until dissolved.

*Chilling.* The oil-acetone solution was chilled rapidly in a continuous stream by running the material through a pilot-plant-size Votator A-unit heat exchanger. The outlet temperature was  $0 \pm 0.5^{\circ}\text{C}$ .

*Crystallization.* The material was run into a set of closed hold-up tanks (pails) in a refrigerated room ( $0 \pm 0.5^{\circ}\text{C}$ .), where it was kept under slow agitation for about 3 hrs. This allowed for sufficient crystallization. In order to maintain a constant crystallization temperature, additional cooling coils have to be installed in large-capacity holding tanks, to offset the heat of crystallization.

Another possibility would be a refrigerated continuous hold-up system, e.g., a tank with baffles or a pipe system.

*Pumping.* As soon as the crystallization had reached the desired level, the material was pumped to the separating device. Since fat crystals are of a semisolid state and can easily be demolished or broken up, centrifugal or gear pumps are unsuitable for this purpose. Air pressure, applied directly to the closed holding tanks, or diaphragm pumps can be used. In a

TABLE IV

Solvent Winterized Cottonseed Salad Oil Samples from a Continuous Pilot Plant Test

Solvent concentration: 10% acetone I.V. of cottonseed oil: 106.8  
Temperature in cooler:  $-0.5^{\circ}\text{C}$ .

Crystallization time (hrs.).....	3	3.5	4	3.5	3.5
I.V. of salad oil.....	112.1	114.8	112.1	111.4	112.2
Cold test of salad oil (hrs.).....	17	30	28	18	30

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 re-

maining 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.

#### REFERENCES

1. Bailey, A.E., "Industrial Oil and Fat Products," 2nd ed., Interscience Publishers Inc., New York, 1951, pp. 868–869.
2. Bailey, A.E., Feuge, R.O., Kraemer, E.A., and Bauer, S.T., *Oil and Soap*, 20, 129–132 (1943).
3. Boucher, R.E., and Skau, E.L., *J. Am. Oil Chemists' Soc.*, 32, 497–501 (1955).
4. Boucher, R.E., and Skau, E.L., *J. Am. Oil Chemists' Soc.*, 29, 455–456 (1952).
5. Boucher, R.E., and Skau, E.L., *J. Am. Oil Chemists' Soc.*, 28, 483–487 (1951).
6. Cavanagh, G.C., *J. Am. Oil Chemists' Soc.*, 33, 528–531 (1956).
7. Cavanagh, G.C., (Ranchers Cotton Oil), U.S. 2,883,405 (1959).
8. Cording, J. Jr., Willard, M.J. Jr., Edwards, P.W., and Eskew, R.K., *J. Am. Oil Chemists' Soc.*, 30, 66–70 (1953).
9. Cording, J. Jr., Willard, M.J. Jr., Edwards, P.W., and Eskew, R.K., *J. Am. Oil Chemists' Soc.*, 30, 111–113 (1953).
10. Muckerheide, V.J. (Emery Industries Inc.), U.S. 2,514,608 (1950).
11. Rubin, L.J. (Canada Packers Ltd.), Canada 565,911 (1958).
12. Rubin, L.J. (Canada Packers Ltd.), U.S. 2,910,363 (1959).
13. Singleton, W.A., and Chandler, C.J., "A New Process for Low-Temperature Fractional Crystallization of Fats and Fatty Acids," given at the A.O.C.S. meeting, New Orleans, 1959.
14. Skau, E.L., Dopp, W.N., Burleigh, E.G., and Banowitz, L.F., *J. Am. Oil Chemists' Soc.*, 27, 556–564 (1950).

[Received October 17, 1960]

## The Oxyethylation of Dinonylphenol

R.C. MANSFIELD, J.E. LOCKE, and K.A. BOOMAN, Research Laboratories, The Rohm and Haas Company, Bristol, Pennsylvania

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