SECTION A-A

used to adjust the amount of current passing through the heating element.

Owing to the relatively slow transfer of heat from the heating block to the test solutions, it is necessary to hold the block at a slightly higher temperature than that desired in the tubes. The transfer of heat was improved slightly by coating the insides of the holes in the block with heat resisting flat black enamel, but there was still a temperature differential between the block † and the solutions. For this apparatus a block temperature of 181° ± 0.2°C. maintained a temperature of 180° ± 0.2°C. in the tubes containing the isomerization solutions, with a temperature difference of less than 0.1°C. among the three tubes. A constancy of ± 0.5°C. has been found satisfactory for the isomerization reaction (1). The block came to 181°C. in 30 min. and the solutions came to 180°C. in 25 min. after the tubes were inserted in the heated block. The solutions could be brought to 180°C. in about 15 minutes if the thermoregulator were bypassed for one to two minutes immediately after the tubes were inserted.

REFERENCES

1. Brice, B. A., Swain, M. L., Schaeffer, B. B. and Ault, W. C., Oil and Soap, 22, 219 (1945).

2. Mitchell, J. H., Kraybill, H. R., and Zscheile, F. P., Ind. Eng. Chem., Anal. Ed., 15, 1 (1943).

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† Although a brass block was used because brass is easy to drill, aluminum has a higher heat capacity and thermal conductivity; the differential between the temperatures of the block and sample might be reduced somewhat if aluminum were used.

Polymerization of Drying Oils. V. Further Observations on the Reaction of Unsaturated Dibasic Anhydrides With Methyl Linoleate[1]

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THIS paper reports the results of experiments on the condensation of methyl linoleate with itaconic and citraconic anhydrides and the reaction of the condensation products with ethylene diamine. Experiments on the condensation of methyl linoleate and maleic anhydride in the presence of dimethylaniline are also described.

In a previous communication (5) it was shown that the reaction product of one mole of methyl linoleate and two moles of maleic anhydride could be separated

into two components. One component, volatile in the molecular still, appeared to be a monoadduct containing one mole of methyl linoleate and one of maleic anhydride. The other component, non-volatile in the molecular still, had properties indicating that it was a polymeric adduct of two moles of methyl linoleate and three of maleic anhydride. This polymeric adduct was found to give gelled products when treated with ethylene diamine.

The experiments with itaconic and citraconic anhydrides were undertaken with the expectation that these anhydrides, considered as substituted maleic anhydrides, would show a reduced reactivity towards methyl linoleate. It was thought that such lowered reactivity might prevent the formation of polymeric adducts and increase the yield of monoadduct.

Although reaction with methyl linoleate occurred to the extent of 46.3% with itaconic anhydride and only 27.6% with citraconic anhydride, both monoadducts and polymeric adducts were obtained from the condensation products. The polymeric adducts were however not as reactive toward ethylene diamine as was the polymeric maleic adduct, and it was possible to achieve a moderate extent of reaction before gelation occurred.

Free and combined itaconic and citraconic anhydrides were differentiated by methods previously employed for maleic anhydride (5). Although not ideal, these methods proved adequate to support the conclusion that both monoadducts and polymeric adducts were formed. It was however not advisable to attempt interpretation of the data for the polymeric adducts in terms of the relative amounts of linoleate and anhydride combined therein.

Analysis of the fractions obtained by molecular distillation showed the apparent persistence of comparatively large amounts of free itaconic and citraconic anhydrides. However it was evident from the data in Table I that the largest amounts of free anhydride were found in those fractions containing the largest amounts of reaction product and that redistillation of volatile fractions concentrated free anhydride in the less volatile fraction rather than in the more volatile fractions as would be expected from the low boiling points of the anhydrides. It was therefore concluded that the analytical evidence indicating free anhydride in the fractions resulted mainly from a response of combined anhydride to the conditions used for determination of free anhydride.

When the non-volatile adducts were heated at 170° with ethylene diamine, gelation occurred in one hour with the itaconic adduct and in 3.5 hours with the citraconic adduct. This behavior contrasts sharply with the behavior of the corresponding maleic adduct, which was found (5) to produce a gel in 6 to 14 minutes at 170°.

Monomeric distillate from the Norelac process (4) was condensed with citraconic anhydride. The yield of condensation product was about 16 grams from 50 grams of monomeric distillate. When heated with ethylene diamine, the polyamide formed was still fusible and soluble in chloroform after 20 hours at 180°. At room temperature the resin was tough and tacky.

It thus appears that about one-fourth of the monomeric distillate, now produced during manufacture of Norelac, could be converted into polyamide resin through its condensation product with citraconic anhydride. The cost of such a process should not differ greatly from the cost of preparing Norelac from soybean oil except for the cost of the citraconic anhydride involved. At present, citraconic anhydride is relatively expensive and is manufactured in small quantities for research purposes. The properties of the new resin suggest that it may be somewhat inferior to standard Norelac and that its commercial value would not justify an increased cost of manufacture. It should however be noted that citraconic anhydride is potentially a cheap chemical should its uses justify large-scale manufacture.

Experiments were also conducted to determine the effect of dimethylaniline on the condensation of maleic anhydride and methyl linoleate. These experiments were based upon an observation of Bruckner and Kovacs (2) who found that small amounts of dimethylaniline suppressed the formation of hetero polymers in the reaction of anethole and maleic anhydride.

Methyl linoleate and maleic anhydride were used in a 1:1 molecular ratio to suppress further the formation of adducts containing more than one maleic residue. The amount of dimethylaniline was varied from 0 to 5%. The results of these experiments are given in Table II. It may be noted that increasing the amount of dimethylaniline caused a decrease in the total yield of reaction product and an increase in the yield of solid reaction product.

TABLE I

Distillation of Adducts of Methyl Linoleate and Itaconic and Citraconic Anhydrides

Fraction	Conditions of collection Temperature, °C.	Pressure	Wt., g.	Unreacted anhydride, %	Neutral Equiv.	Sap. Equiv.	I.V.
Itaconic Adduct [1]		microns					
1	50	4-10	8	1.7	5232	238	169.2
2	100	3-5	11	2.0	1660	211	161.9
3	150	3-5	10	5.9	460	159	110.8
3a[2]	50	3-5	0.7	0.5	6997	461	172.0
3b[2]	110	3-5	2.3	6.2	357	169	114.0
4	Non-volatile	Non-volatile	14	14.1	232	118	50.5
Citraconic Adduct [3]		mm.					
1	90	10	1.0	64.2	....	....	....
2	200	10	11.0	95.0	5882	59.4	2.2
		microns					
3	50	10-20	3.2	1.0	3049	296	168.2
4	100	4-12	16.5	4.6	984	244	155.5
5	150	3-5	11.0	8.7	349	141	94.7
5a[4]	50	3-5	1.9	2.6	1396	268	159.5
5b[4]	100	3-5	4.4	9.7	234	132[5]	86.5
6	Non-volatile	Non-volatile	20.0	8.6	230	135[6]	39.9
Theoretical[7]	......	......	......	......	204	136	125[8] (62.5)

[1] An additional 10 g. was recovered by washing still between passes.
[2] Fractions obtained by redistilling 4.6 g. of Fraction 3.
[3] An additional 7 g. was recovered by washing still between passes.
[4] Fractions obtained by redistilling 9.7 g. of Fraction 5.
[5] Molecular wt. 365 by Signer's method (3).
[6] Molecular wt. 750-910 by Signer's method (3).
[7] For either monoadduct. Compare with data for Fractions 3b and 5b. Calc'd mol. wt. 406.6.
[8] Calculated values for one and two double bonds.

TABLE II

Condensation of Methyl Linoleate and Maleic Anhydride in the Presence of Dimethylaniline

DMA[1]	Yield of solid product[2]	Yield of liquid product[2]	Methyl linoleate recovered[2]	Unreacted maleic anhydride[2,3]
%	%	%	%	%
0.0	1.8	53.2	18.6	....
0.05	2.8	52.9	21.5	5.5
0.5	2.7	40.6	28.9	5.5
5.0	9.1	23.3	30.9	2.4

[1] Dimethylaniline.
[2] Expressed as per cent of charge.
[3] In liquid portion of crude adduct before separation of unreacted materials.

As shown in Table III, the liquid reaction products gave approximately the same values for neutralization equivalent, saponification equivalent, and methoxyl content. The average values agree well with those expected for an adduct containing three molecules of maleic anhydride and four of methyl linoleate. The discrepancy in methoxyl content is not considered serious since it was shown previously (5) that methoxyl groups are difficult to remove from compounds of this type by the customary analytical method. The liquid reaction products were very vis-

TABLE III

Properties of Liquid Adduct

DMA[1]	Viscos- ity[2]	Neutral equiv.	Sap. equiv.	OCH₃	Mol. wt.[3]
%				%	
0.0	Z₆	238.7	138.5	6.06	1000
0.05	Z₆	247.7	147.4	6.04	1490
0.5	Z₆	242.7	152.7	6.13	1210
5.0	Z₆	243.8	158.2	7.31	1490
Average	....	243.2	149.2	6.38	1298
Calculated[4]	....	246	147	8.42	1472

[1]Dimethylaniline.
[2]Gardner Scale.
[3]Signer's Method (3).
[4]For an adduct containing three molecules of maleic anhydride and four of methyl linoleate.

cous (ca. Z_6) and were therefore not submitted to molecular distillation.

Table IV shows the analytical results obtained for the solid reaction product. The high melting points, the low neutralization and saponification equivalents, and the significant methoxyl content indicate that these solid products are heteropolymers of maleic anhydride and methyl linoleate.

TABLE IV

Properties of Solid Product

DMA[1]	Neutral equiv.[2]	Sap. equiv.[2]	OCH₃	N	M.P.[3]
%			%	%	
0.0	80.1	83.0	4.93	0.00	>250[4]
0.05	66.6	54.7	2.73	0.00	Chars 230° vaporizes 260°-270°
0.5	76.1	91.6	2.01	0.24	Does not melt
5.0	......	67.6	3.22	0.94	Does not melt

[1]Dimethylaniline.
[2]Calculated value for maleic anhydride, 49; for maleic or fumaric acid, 58.
[3]In capillary, uncorrected.
[4]M.P. on micro hot stage 220°-225°.

Experimental

Starting Materials: Methyl linoleate was prepared by the customary debromination procedure: I. V., 169.2; calc'd 172.3.

Itaconic anhydride was prepared by a modification of the method of Anchutz and Petri (1). Itaconic acid and acetyl chloride (3 mols. of acetyl chloride per mol. of itaconic acid) were refluxed until the acid had completely dissolved (about 2.5 hours). The reaction mixture was cooled in "Dry-Ice" and filtered. An additional crop of crystals could be obtained by further chilling of the filtrate. The colorless crystals were washed with ether and dried; M. P. 67°-68°; yield, 88%. Anchutz and Petri gave M. P. 68°.

The citraconic anhydride was a commercial preparation, b.p. 110.0°-110.5° at 20-25 mm. It was used without further purification. The maleic anhydride was Eastman's "White Label" grade.

Condensation of Itaconic Anhydride and Methyl Linoleate: Methyl linoleate (42 g.; 1 mol.) and itaconic anhydride (32 g.; 2 mols.) were heated for 8 hours at 200°C. in an atmosphere of carbon dioxide. About 25 g. of benzene was used to rinse the apparatus, giving a total of 90 g. of the benzene solution of the reaction mixture which was separated from about 6 g. of a resinous material insoluble in benzene. The benzene solution was analyzed by the previously described method (5), modified to provide mechanical shaking for 2 hours. The solution was found to contain 17.2 g. of unreacted itaconic acid, indicating that about 46% of the anhydride had reacted. The ben-

zene solution was then distilled, first at atmospheric pressure to remove benzene and then at 5 mm. to a pot temperature of 240° to remove unreacted itaconic anhydride and methyl linoleate. All distillate at 5 mm. was collected in one fraction weighing 6 g. and containing 93.4% of free itaconic anhydride. Neutralization equivalent of this fraction was 62.1. The residue was distilled in a falling film molecular still with the results given in Table I.

Unreacted itaconic anhydride and neutralization equivalents were determined by previously described methods (5). Saponification equivalents were obtained by refluxing 3 hours with alcoholic potassium hydroxide, and iodine numbers were determined by the half-hour Wijs method. Fractions 1 and 2 are apparently recovered methyl linoleate. Fraction 3 is the monoadduct, and the residue, the polymeric adduct. In this experiment 65 g. out of 74 g. of initial material are accounted for.

Fraction 3 was redistilled by passages through the molecular still at 50° and 100°. The data are given in Table I. Fraction 3a represents an additional recovery of methyl linoleate. Fraction 3b is purified monoadduct. It is noteworthy that Fraction 3b apparently contains more unreacted itaconic anhydride than did original Fraction 3.

Condensation of Citraconic Anhydride and Methyl Linoleate: This condensation was conducted with the same weights of reactants and by essentially the same procedure as the itaconic condensation. One modification was made in that benzene used for rinsing the apparatus was removed before determination of unreacted anhydride. The reaction mixture was found to contain 9.8 g. of unreacted citraconic anhydride. It was distilled at 10-mm. pressure to a pot temperature of 250°. The residue was then passed through the molecular still. Data for the fractions obtained are given in Table I. Fractions 1 and 2 are principally unreacted citraconic anhydride. Fractions 3 and 4 are mainly recovered methyl linoleate. Fraction 5 is the monoadduct, and the residue, the polymeric adduct. In this experiment 69.7 g. out of 74 g. of initial material is accounted for.

Fraction 5 was redistilled in the molecular still. The results, given in Table I, are similar to those obtained in the itaconic condensation.

Preparation of Polyamides: The polymeric adduct (2.3 g.) was mixed with 2.1 ml. of 70.1% aqueous ethylene diamine and heated to 170° with constant stirring in an atmosphere of nitrogen. The polyamide from the itaconic adduct gelled at the end of one hour whereas that from the citraconic adduct gelled at the end of 3.5 hours.

Preparation of a Polyamide From Monomeric Distillate: The sample of monomeric distillate used had an iodine value of 90.4 and contained 11.7% of saturated ester, 67.2% of oleate, and 11.3% of linoleate determined spectrophotometrically. It contained 4.8% of diene conjugation. The amount of citraconic anhydride used was calculated on the mole-per-mole basis, assuming an average molecular weight of 296.5 for monomeric distillate. Inasmuch as the saturates present should not react, this procedure gave approximately 17% excess over the amount equivalent to the reactive components.

A 50-g. sample of the monomeric distillation and 18.9 g. of citraconic anhydride were heated for 8 hours at 200° in an atmosphere of nitrogen. Unre-

acted material (50.3 g.) was removed by distillation at 0.3-0.4 mm. pressure. The residue of condensation product (15.6 g.) had an iodine value of 63, a neutralization equivalent of 326, and contained 6.2% unreacted citraconic anhydride.

A mixture of 2.5 g. of this condensation product and 1.7 g. of a 69% aqueous solution of ethylene diamine was heated at 170°-180° for 20 hours. During this time the mixture was stirred by bubbling nitrogen through it. The product was a tough, tacky resin soluble in acetone and chloroform.

Condensation of Methyl Linoleate and Maleic Anhydride in the Presence of Dimethylaniline: Condensation was effected between 25 g. (1 mol.) of methyl linoleate and 8.3 g. (1 mol.) of maleic anhydride in the presence of 0.0%, 0.05%, 0.5%, and 5.0% of dimethylaniline. Percentages of dimethylaniline were based on the total weight of the reaction mixture.

In each case the reaction mixture was heated for 8 hours at 200° in an inert atmosphere. After cooling, the reaction mixture was filtered to remove a solid reaction product. The filtrate was distilled at reduced pressure to remove unreacted materials. Data on yields are given in Table II. Analytical data for the distillation residue are given in Table III. The solid reaction product was purified for analysis by washing with benzene. Table IV shows the analytical results. The solid product from the reaction containing 5.0% of dimethylaniline was insoluble in pyridine and the neutralization equivalent is not reported for this material. Saponification equivalents were obtained by heating the sample for 6 hours at 170°-180° with a 0.1 N solution of potassium hydroxide in diethylene glycol. Potentiometric titration was required because of the dark color developed.

Summary

Adducts of methyl linoleate with itaconic and citraconic anhydrides have been prepared. Each adduct was separated into monomeric and polymeric components. With ethylene diamine, the itaconic and citraconic polymeric adducts gave gelled products at 170° in one hour and 3.5 hours, respectively. The adduct of citraconic anhydride and monomeric distillate gave a tough, tacky resin which did not gel during a reaction time of 20 hours at 170°-180°.

The effect of dimethylaniline on the condensation of methyl linoleate and maleic anhydride was studied. Increasing amounts of dimethylaniline were found to promote the formation of a heteropolymer and to decrease the yield of liquid adduct.

REFERENCES

1. Anschutz, R., and Petri, W., Ber. *13*, 1539 (1880).
2. Bruckner, V., and Kovacs, J., Nature *161*, 651 (1948).
3. Clark, E. P., "Semimicro Quantitative Organic Analysis," p. 78, Academic Press, New York (1943).
4. Falkenburg, L. B., Teeter, H. M., Skell, P. S., and Cowan, J. C., Oil and Soap *22*, 143-148 (1945).
5. Teeter, H. M., Geerts, M. J., and Cowan, J. C., J. Am. Oil Chemists' Soc. *25*, 158-162 (1948).

Fatty Acid Distillation—Comparison of Two Column Types

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THE fractionation of fatty acids is an example of the increasing application of vacuum distillation.

Although many papers have been published on the theoretical and practical aspects of petroleum fractionation, few have been directed to the theory, practice, and design of equipment for the fractionation of fatty acids. Equipment for fractional distillation of fatty acids has been described by Potts and McKee (12) and by Potts (11). Norris and Terry (8) treat the laboratory fractionation of fatty acids, and the literature on this subject has been reviewed by Bailey (1) and by Ralston (13). Vapor pressure data for saturated n-alkyl acids are given by Pool and Ralston (10), and Monick, Allen, and Marlies (6) give equilibrium data for lauric acid-myristic acid, methyl laurate-lauric acid, and methyl palmitate-methyl stearate.

In the study of distillation equipment design it is first necessary to have vapor-liquid equilibrium data for the materials being separated. It is the object of this paper to present the vapor-liquid equilibrium curves for lauric acid-myristic acid, myristic acid-palmitic acid, and palmitic acid-stearic acid, and to compare the performance of a bubble-cap column with that of a packed column with fibrous glass packing in separating these materials.

Equipment

Still. The still used for measuring the vapor-liquid equilibrium compositions was similar to that used by Gillespie (4). It is shown in Fig. 1. Heat is supplied to the material in the boiler by the heater, causing vaporization. The vapors entrain liquid, and the liquid and vapor remain in contact and come to equilibrium as they pass up the Cottrell tube to the disengagement chamber. Here the liquid and vapor are separated, the liquid returning to the boiler, the vapors passing to the condenser. The vapors are condensed and the condensed liquid is collected in the condensate trap, from which it overflows to the boiler. The stream of hot liquid separated from the vapor in the disengagement chamber is combined with the condensed vapor before its return to the boiler. Overflow from the condensate trap is returned to rejoin the liquid through a drop-counter and capillary; this gives a small hold-up and a constant rate of flow.

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