occurs, followed by a 2 p.s.i. or greater drop in the succeeding hour.

The Oxygen Bomb Method has been used quite effectively in the laboratory to develop information on the oxidative characteristics of a wide variety of products. The wide applicability of this method in the food industry has been demonstrated by successful evaluations of products such as fish scrap, fried chicken, various types of nuts, egg solids, butter oil, fish sticks, pastry and cake premixes, and fatty acids. A number of other materials not successfully evaluated with present techniques, possibly because of low fat content or extreme stability of oxidizable components, are some cereal products, some animal feeds, coffee, and some candies.

Summary

The use of a dispersing agent to expand the surface area, thus providing an increase in reactivity of fats and oils under the conditions of the test, has been investigated. This dispersion technique permits the testing of a wider range of products, decreases the test time, and results in sharper end-points. These improvements should serve to increase the applicability of the Oxygen Bomb Method as a tool for oxidation studies and quality control in the food industry. A general comparison of the Oxygen Bomb Method with the AOM and Schaal Oven Method has been presented to illustrate the relationship between results obtained by these various methods. The dispersion technique has been combined with previously established bomb techniques, and procedures for testing a wide variety of fats, oils and food products by the Oxygen Bomb Method are suggested.

REFERENCES

1. A.S.T.M. Committee D-2, "A.S.T.M. Standards on Petroleum Products and Lubricants," 254–257 (1955).
2. Gearhart, W. M., Stuckey, B. N., and Austin, J. J., J. Am. Oil Chemists' Soc., *34*, 427–430 (1957).
3. Joyner, N. T., and McIntyre, J. E., Oil and Soap, *15*, 184–186 (1938).
4. King, A. E., Roschen, H. L., and Irwin, W. H., Oil and Soap, *10*, 103–109 (1933).
5. Riemenschneider, R. W., Turen, J., and Speck, R. M., Oil and Soap, *20*, 169–171 (1943).

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Plasticizer Properties of Some Acrylonitrile-Eleostearate Adducts and Their Hydrogenated Derivatives

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IN AN EARLIER PUBLICATION (1) we have described the Diels-Alder reaction of the *n*-butyl esters of *alpha*- and *beta*-eleostearic acids with acrylonitrile and fumaronitrile and at the same time have reported the plasticizer properties of the adducts. It was found that acrylonitrile reacts readily with the eleostearates and that the resulting products, although not entirely suitable as primary plasticizers, were quite satisfactory as secondary plasticizers. In conjunction with dioctyl phthalate or tricresyl phosphate the acrylonitrile adducts contributed a number of desirable features to the vinyl chloride-vinyl acetate copolymer.

In view of these considerations it appeared of importance to ascertain whether or not the plasticizing qualities could be improved by modification of the acrylonitrile adduct to produce a material with suitable properties as a primary plasticizer.

It was observed that the presence of appreciable amounts of a polyunsaturated or of a completely saturated, long-chain moiety impairs compatibility (2), particularly in glyceridic materials (3). Improved compatibility results from the reduction of polyunsaturation. Saturation of the cyclic and exocyclic ethylenic linkages of certain adducts of the eleostearates also results in an enhanced compatibility of the material (4). Accordingly an investigation was undertaken to establish optimum conditions for the hydrogenation of the ethylenic bonds of the acrylonitrile adducts with minimum reduction of the nitrile group and to determine the plasticizing properties of the hydrogenated derivatives.

Experimental

The procedures employed for the preparation of the esters of tung oil fatty acids, acrylonitrile adducts of the eleostearic acid esters, and selective hydrogenation of these adducts were essentially the same for the methyl, ethyl, and butyl derivatives. A typical series of experiments is described in detail.

Preparation of the Esters of Tung Oil Fatty Acids. Tung oil (1,200 g.) was added to a solution of sodium alcoholate, which had been prepared previously by dissolving metallic sodium (6.6 g.) in the appropriate absolute alcohol (400 g.). This mixture was refluxed with frequent shaking over a period of 2 hrs. The glycerol layer which separated from the reaction product on cooling was removed, and the crude esters were washed successively with two 500-ml. portions of N/2 HCl and then with several 250-ml. portions of water until free of acid. The esters were freed from volatile materials by vacuum-stripping on a steam cone, employing a stream of carbon dioxide. The resulting product was distilled through a short-path column at reduced pressure, yielding a main fraction which weighed approximately 875 g. The products obtained had the following characteristics: methyl esters—b.p. 152°C./5 microns, n_D^{20} 1.4925, 73% methyl *alpha*-eleostearate, 3% methyl *beta*-eleostearate;[2] ethyl esters—b.p. 156°C./100 microns, n_D^{20} 1.4928, 49% ethyl *alpha*-eleostearate, 18% ethyl *beta*-eleostearate; butyl esters—b.p. 173°C./350 microns, n_D^{20} 1.4915, 60% butyl *alpha*-eleostearate, 4% butyl *beta*-eleostearate.

The esters were stabilized with 0.05% of hydroquinone and stored in a refrigerator at 5°C. until required.

Reaction of Acrylonitrile with the Eleostearates. A mixture of 250 g. of the appropriate esters (*ca.* 0.65 mole), 75 g. of acrylonitrile (1.40 moles), and 1 g. of hydroquinone was refluxed for 96 hrs. At this time

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[2] Eleostearates were determined by the method of Hoffman *et al.* (5).

the ultraviolet analysis for unreacted eleostearate in the reaction mixture indicated that the conversion was about 90% complete. The excess acrylonitrile was removed by vacuum-stripping on a steam cone, employing a stream of carbon dioxide. The adduct was fractionally distilled under high vacuum, and the fractions which had similar boiling ranges were combined (*ca.* 125 g.) and stored under dry nitrogen at −20°C. The following adducts were prepared: methyl eleostearate-acrylonitrile: boiling range 166–170°C./30 microns, 88% yield; ethyl eleostearate-acrylonitrile: boiling range 178–181°C./30 microns, 88% yield; butyl eleostearate-acrylonitrile: boiling range 184–188°C./30 microns, 91% yield. Nitrogen analyses[3] reported in Table I indicated these products to be of about 96% purity.

A reaction of acrylonitrile with tung oil, containing 73% *alpha*-eleostearic acid, carried out under the same conditions, was 96% complete. This product was not distilled.

Hydrogenation of the Ethylenic Bonds of the Acrylonitrile Adduct. Each sample, approximately 0.1 mole of the adduct, was hydrogenated at room temperature in a Parr hydrogenation apparatus, using 150 ml. of absolute methanol as a solvent and 3 g. of 10% palladium on carbon as a catalyst. The hydrogenation was initiated at approximately 30 lbs. pressure and was continued until the rapid uptake of hydrogen ceased. About 30 minutes were required each time to hydrogenate the one cyclic and one exocyclic ethylenic bonds of the adduct. During this time the calculated amount of hydrogen (0.2 mole) necessary to saturate the ethylenic bonds was taken up. The hydrogenated product was filtered free of catalyst through a bed of Hyflo Super Cell. The solvent was removed by vacuum stripping by employing a stream of carbon dioxide. The results of the analyses of the various products before and after hydrogenation are presented in Table I.

TABLE I

Comparison of Certain Characteristics of the Acrylonitrile-Eleostearate Adducts Before and After Hydrogenation of the Ethylenic Bonds

Name of adduct	n_D^{20}	% Nitrogen		Absorptivities (a) at 4.44 microns
		Calc.	Found	
Methyl eleostearate-acrylonitrile	1.4850	4.17	3.98	0.03
Hydrogenated methyl eleostearate-acrylonitrile	1.4730	4.01	3.85	0.03
Ethyl eleostearate-acrylonitrile	1.4820	3.85	3.76	0.05
Hydrogenated ethyl eleostearate-acrylonitrile	1.4712	3.75	3.62	0.05
Butyl eleostearate-acrylonitrile	1.4810	3.61	3.51	0.05
Hydrogenated butyl-eleostearate-acrylonitrile	1.4709	3.57	3.45	0.06
Tung oil-acrylonitrile	1.4999	3.08	3.16	......

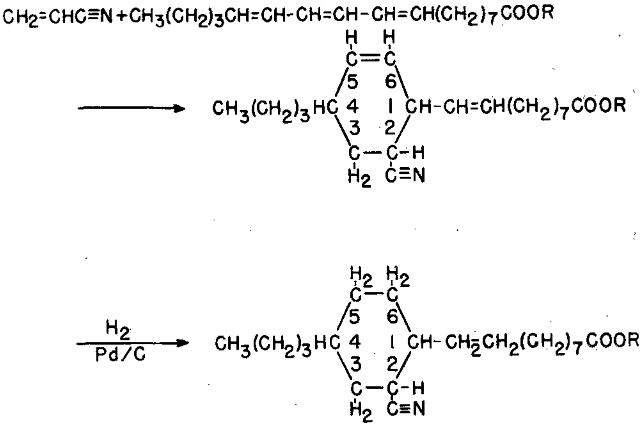
Plasticizer Screening. The acrylonitrile-eleostearate adduct esters and their hydrogenated analogs were screened for their plasticizing characteristics with polyvinyl chloride-polyvinyl acetate copolymer. The following typical formulation was used: resin (Vinylite VYDR), 63.5%; plasticizer, 35.0%; stearic acid, 0.5%; and basic lead carbonate, 1.0%.

In those instances where less than 35% plasticizer was used, the resin content was varied in accordance with the following formula, percentage of resin = (98.5 − x), where x is the percentage of plasticizer. These formulations were milled and molded at 310°F. The detailed procedures followed in these operations as well as the preparation of the test specimen and various tests used have been described previously (6).

Discussion

Previous work has shown that dienophiles add across the *trans,trans* portion of the conjugated triene system present in *alpha*-eleostearic acid (7, 8, 9). Acrylonitrile adds across the 11-*trans*, 13-*trans* ethylenic bonds of the *alpha*-eleostearates, forming two isomeric compounds which contain a cyano group either on the second or third carbon atom of the cyclohexene nucleus and a *cis*-exocyclic ethylene bond in one side chain of the adduct. Inspection of the data presented in Table I reveals that neither the nitrogen content nor the nitrile absorptivity (at 4.4 microns) of the adducts was appreciably altered during the course of the hydrogenation. These data together with the information regarding the amount of hydrogen absorbed lead to the conclusion that the ethylenic bonds of the adducts were preferentially hydrogenated in the presence of the nitrile group. These hydrogenated materials would be expected to have improved stability owing to the absence of ethylenic unsaturation.

The following equation of the Diels-Alder reaction between the *alpha*-eleostearic acid esters and acrylonitrile illustrates the typical schemes of conversion described above as well as the structures of one of the resulting isomers and its hydrogenated derivative (where R represents the methyl, ethyl, or butyl group).



The eleostearic moiety of tung oil would be modified by acrylonitrile in a similar manner to that presented for the simple esters.

The results of the plasticizer screening tests for the acrylonitrile-eleostearate adducts and the hydrogenated acrylonitrile-eleostearate adducts are given in Table II. With the exception of the methyl derivative, the unhydrogenated adducts are incompatible at the 35% level; the ethyl and butyl derivatives showed profuse bleeding after a period of 30 and seven days, respectively. Since the butyl esters of *alpha*- and *beta*-eleostearate-acrylonitrile adducts were shown to be satisfactory as secondary plasticizers (1), it would be expected that the present adducts derived from mixtures of *alpha*- and *beta*-eleostearates would also be satisfactory as secondary plasticizers.

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[3] Kjeldahl method.

TABLE II

Plasticizing Characteristics of the Hydrogenated and Nonhydrogenated Adducts

Plasticizer	Plasticizer (%)	Tensile strength (p.s.i.)	100% Modulus (p.s.i.)	Elongation (%)	Brittle point (°C.)	Compatibility[a] (days)	Volatility loss[b] (%)
Acrylonitrile-eleostearate adduct							
Methyl ester	35	2670	1190	300	−25	150+	0.20
Ethyl ester	30	3140	1540	360	−29	<30	......
	35	........[c]	1210	......[c]	−33	<30	......
Butyl ester	30	3230	1820	330	−29	< 7	......
	35	........[c]	1308	......[c]	−35	< 7	......
Hydrogenated acrylonitrile-eleostearate adduct							
Methyl ester	30	3230	1760	330	−15	150+	......
	35	........[c]	1190	......[c]	−25	150+	0.13
Ethyl ester	30	3150	1550	350	−23	150+	......
	35	........[c]	1290	......[c]	−27	150+	0.13
Butyl ester	35	2840	1350	410	−29	150+	0.16
Tung oil-acrylonitrile adduct	35	2950	2520	190	− 3	150+	0.04
Control (DOP)	30	3270	2180	300	−27	......	......
	35	3030	1600	370	−33	......	0.21

[a] + Indicates no bleeding during time specified. [b] Activated carbon method A.S.T.M. D 1203-52T. [c] Beyond limit measurable on IP-4 tester (6 in.) on 1-in. standard test length.

The hydrogenated adducts, on the other hand, appear to be sufficiently compatible to be used as primary plasticizers with vinyl copolymer at the 35% level. Hydrogenation vastly improved the compatibility of these adducts without changing the other plasticizing characteristics appreciably.

The stocks plasticized with the nonhydrogenated and hydrogenated adducts are inferior in tensile strength, superior in modulus, and comparable in ultimate elongation and brittle point. In most instances they exhibit lower volatility than the stock plasticized with DOP (di-2-ethylhexylphthalate).

The outstanding characteristic of all these adducts is their high plasticizing efficiency, as reflected by the low modulus at 100% elongation. In certain instances, *viz.*, the ethyl and butyl adducts and the hydrogenated methyl and ethyl adducts, it was not possible to determine break and elongation at the standard plasticizer concentration of 35% since the extensibillity of the stock exceeded the limits of the IP-4 Scott Tester. These two properties were therefore evaluated at a lower plasticizer level (30%).

Although the tung oil-acrylonitrile adduct was not found to be the equivalent of DOP in certain respects, it does have the advantage of low volatility and is suitable as a primary plasticizer.

Summary

The addition products obtained by the Diels-Alder reaction of acrylonitrile with the methyl, ethyl, and butyl eleostearates have been prepared in good yields and purified by means of high-vacuum distillation. It has been possible to saturate preferentially by hydrogenation both the cyclic and exocyclic double bonds of the acrylonitrile adducts without material reduction of the nitrile group. Also the acrylonitrile adduct of tung oil has been prepared. All these adducts have been intercompared with DOP and evaluated as primary plasticizers for vinyl chloride-vinyl acetate copolymer. These products, with the exception of the nonhydrogenated ethyl and butyl derivatives, were found to be satisfactory as primary plasticizers. The results obtained indicate that hydrogenation greatly improves the compatibility of the adducts without changing their other plasticizing characteristics appreciably. The outstanding characteristic of all the adducts is their high plasticizing efficiency, as reflected by their low modulus at 100% elongation.

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REFERENCES

1. Hoffmann, J. S., O'Connor, R. T., Magne, F. C., and Bickford, W. G., J. Am. Oil Chemists' Soc., *33*, 410–414 (1956).
2. Magne, F. C., Mod, R. R., and Skau, E. L., Ind. and Eng. Chem., *50*, 617–618 (1958).
3. Magne, F. C., and Mod, R. R., J. Am. Oil Chemists' Soc., *30*, 269–271 (1953).
4. Hoffmann, J. S., O'Connor, R. T., Magne, F. C., and Bickford, W. G., J. Am. Oil Chemists' Soc., *32*, 533–538 (1955).
5. Hoffmann, J. S., O'Connor, R. T., Heinzelman, D. C., and Bickford, W. G., J. Am. Oil Chemists' Soc., *34*, 338–342 (1957).
6. Magne, F. C., and Mod, R. R., Ind. and Eng. Chem., *45*, 1546–1547 (1953).
7. Bickford, W. G. DuPré, E. F., Mack, C. H., and O'Connor, R. T., J. Am. Oil Chemists' Soc., *30*, 376–381 (1953).
8. Paschke, R. F., Tolberg, Wesley, and Wheeler, D. H., J. Am. Oil Chemists' Soc., *30*, 97–99 (1953).
9. Alder, K., and Kuth, R., Ann., *609*, 19–39 (1957).

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Isolation of Two Nitrogen-Free Toxins from Tung Kernels

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TUNG MEAL AND OIL are produced from the seeds of the trees *Aleurites fordii* and *A. montana*. The meal is highly toxic to animals, including man, and has found little use except as a nitrogenous fertilizer. It contains 22–25% proteins and is a potentially valuable feedstuff. The program under which this research was conducted has as its goal the upgrading of tung meal by detoxifying it to render it acceptable as an animal feed.

Mann, Hoffman, and Ambrose (5) and Balthrop, Gallagher, McDonald, and Camariotes (1) recently reviewed the literature on the toxicity of tung kernels and meal. The consensus is that there are at least two toxic substances in the tung kernel. One of these

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