



Chart 2. Individual plant oil retentions, Clay 4 vs. Clay 6.

Chart 1 plots oil retention *vs.* ABD for both laboratory results and the average of the seven plant tests involving Clays 4 and 6. Chart 2 plots the individual oil retention *vs.* ABD for the seven plant tests.

It will be observed from Chart 1 that in the case of the laboratory results a reasonably consistent inverse relationship occurred between ABD and oil retention. Also the plant average figures for Clays 4 and 6 paralleled the laboratory curve.

From Chart 2 it will be noted that while the individual plant results on the two clays paralleled the laboratory curve, the oil retentions between plants varied considerably from each other on the same clay. On Clay 4, for example, the retentions varied from 27.8 to 38.4%, on Clay 6 from 35.4 to 46.6%. This is consistent with experience and is the result of different filtration conditions, types of filter-press, and methods of press-blowing between plants.

If the refiner knows that Clay A has a given average oil-retention and ABD over a period of time, he can estimate the oil retention he should obtain with Clay B with a fair degree of accuracy simply by paralleling the laboratory curve in Chart 1 with the ABD of Clay B. Thus, if Clay A has an average oil-retention of 50% and an average ABD of 54 lb. per cu. ft., Clay B with an ABD of 60 lb. per cu. ft. should give an oil retention of 42%.

Summary

Data have been presented which demonstrate that the inverse relationship is reasonably consistent between the apparent bulk density of a bleaching clay and its oil retention.

REFERENCES

1. "Industrial Minerals and Rocks," pp. 128, 216, 2nd ed., The American Institute of Mining and Metallurgical Engineers, New York (1949).
2. Langston, R., and Rich, A. D., *Am. Oil Chemists' Soc.*, **23**, 182 (1946).
3. Nutting, P. G., "Adsorbent Clays: Their Distribution, Properties, Production, and Uses," U. S. Geol. Survey Bull. 928-C (1943).
4. Ries, H., "Clays, Their Occurrence, Properties, and Uses," 3rd ed., John Wiley and Sons Inc., New York (1927).

[Received November 4, 1959]

Tung Oil Derivatives as Plasticizers for Buna-N Rubber

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NITRILE RUBBER, an oil-resistant acrylonitrile-butadiene copolymer, has been manufactured in the United States since 1939. In order to satisfy the demand by industry today, nitrile rubber is being produced under several different trade names at the rate of hundreds of tons per day. The properties of the vulcanized polymer can be widely varied by changing the ratio of butadiene to acrylonitrile as well as by using different compounding ingredients (1). The type of softener or plasticizer employed often has the ability to impart (to the nitrile rubber stocks) special properties which might be desired by various industries. In general, softeners are used for controlling the hardness and low-temperature flexibility of the materials.

In order to extend the utilization of tung oil and to make available a new source of raw materials, research has been directed toward the development of new chemical derivatives of tung oil suitable as plasticizers or Buna-N rubber softeners. Tung oil is a

triglyceride which contains as glycerides approximately 75% of *alpha*-eleostearic (9,11,13-octadecatrienoic) acid and small percentages of other monoethenoic, dienolic, and saturated fatty acids (2). It has been reported in previous publications from this laboratory that Diels-Alder addition products of certain dienophiles and various esters of the eleostearic acids were satisfactory as primary plasticizers for vinyl chloride-vinyl acetate copolymer (3,4,5,6). Although the adducts of the tung oil itself were not generally compatible as primary plasticizers for polyvinyl chloride, their production is economical because of the limited number of operations required. Since many of these materials contain a number of ester linkages which tend to enhance the compatibility of fatty acids with polar rubbers, such as the nitrile type, it appeared of interest to investigate their suitability as softeners for Buna-N rubber. This paper will describe the preparation and properties of the methyl vinyl ketone, dimethyl maleate, methyl acrylate, and acrylonitrile adducts of tung oil as well as their hydrogenated counterparts and will discuss their plasticizing characteristics for Buna-N rubber.

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TABLE I
 Physical Characteristics of Buna-N Stocks Plasticized with Derivatives of Tung Oil

Plasticizers	Ultimate elongation (%)		300% Modulus (p.s.i.)		Tensile strength (p.s.i.)		Hardness Shore A (10 sec.)	Weight loss ^a (%)	Volume change ^b (%)	Brittle point (°C.)	Compatibility (days) ^c
	Unaged	Aged ^a	Unaged	Aged ^a	Unaged	Aged ^a					
Tung oil adduct											
Methyl vinyl ketone.....	810	680	740	1200	2160	2390	44	0.53	30.3	-36	90+
Dimethyl maleate.....	810	650	820	1460	2330	2500	43	1.39	24.6	-44	90+
Methyl acrylate.....	780	640	780	1380	2270	2550	43	1.79	24.1	-40	90+
Acrylonitrile.....	810	600	820	1200	2290	2110	42	0.41	29.3	-40	90+
Hydrogenated tung oil adduct											
Methyl vinyl ketone.....	740	650	1010	1570	2390	2480	45	0.47	34.6	-40	14 ^d
Dimethyl maleate.....	660	520	1130	1920	2410	2640	45	1.72	23.2	-44	90+
Methyl acrylate.....	690	560	1090	1700	2480	2630	45	2.00	21.7	-48	90+
Acrylonitrile.....	680	550	1080	1590	2320	2390	45	0.43	31.0	-36	21 ^d
Dibutyl sebacate (control).....	680	530	1100	1970	2420	2660	45	5.34	19.9	-52	90+

^a Aged in forced draft oven at 212°F. for 48 hrs. ^b Immersed 72 hrs. in mixed solvent at 78°F. ^c Indicated no exudation during time specified. ^d Smearred on contact.

Experimental

MATERIALS

Tung Oil. Domestic tung oil containing 75.2% of trienoic acids was used: I.V. (hydrogenation), 228.0; $n^{20/D}$, 1.5195.

Dienuophiles. Methyl vinyl ketone, maleic anhydride, beta-propiolactone, and acrylonitrile were, all of commercial origin, used without further purification.

Methyl Vinyl Ketone-Tung Oil Adduct. Two batches of this material, each employing 100 g. of tung oil, 50 g. of methyl vinyl ketone, 0.2 g. of hydroquinone, and 100 ml. of benzene were prepared by the method described for the adduction of the methyl esters of tung oil fatty acids (6). After the solvent and excess methyl vinyl ketone were stripped off, the reaction product was filtered while still hot through a thick porous filter paper. The resulting methyl vinyl ketone-tung oil adduct (235 g.) had: carbonyl O, 4.1%; I.V. (hydrogenation), 126.6; sap. equiv., 343.6; $n^{20/D}$, 1.4949.

Dimethyl Maleate-Tung Oil Adduct. A mixture of 200 g. of tung oil, 70 g. of powdered maleic anhydride, and 0.2 g. of hydroquinone was stirred by a magnetic stirrer and slowly heated under an atmosphere of carbon dioxide. When the temperature reached 54°C., an exothermic reaction set in, raising the temperature to 144°C. Heating was immediately discontinued, and the product was allowed to cool gradually while the stirring and carbon dioxide atmosphere were continued. The product was then dissolved in 1,000 ml. of benzene, washed with six 300-ml. portions of water to remove excess maleic anhydride, and finally dried over anhydrous sodium sulfate. The benzene was removed by distillation, first at atmospheric pressure and finally under high vacuum, yielding 246 g. of product. A 160-g. portion of this adduct was esterified in the usual manner employing 1,500 ml. of methanol, which contained 15 ml. of concentrated sulfuric acid. The recovered ester, after being filtered through a bed of Hyflo Super Cel, had the following constants: I.V. (hydrogenation), 112.6; sap. equiv., 272.0; $n^{20/D}$, 1.4815.

Methyl Acrylate-Tung Oil Adduct. The acrylic acid-tung oil adduct was prepared in a manner similar to that described for the butyl esters of tung oil fatty acids (3). In this case 180 g. of tung oil, 40 g. of beta-propiolactone, 0.4 g. of potassium carbonate, and 0.2 g. of hydroquinone were heated at 200°C. for 3 hrs. under an atmosphere of carbon dioxide. The product was dissolved in 1,000 ml. of ether, washed with three 300-ml. portions of water to remove the excess propiolactone, and dried over anhydrous so-

dium sulfate (yield 208.5 g.). The adduct (201.5 g.) was esterified with methanolic sulfuric acid as described above for the dimethyl maleate adduct of tung oil. The recovered ester, after being filtered through a bed of Hyflo Super Cel, had the following constants: I.V. (hydrogenation), 119.9; sap. equiv., 237.2; $n^{20/D}$, 1.4778.

Acrylonitrile-Tung Oil Adduct. This material was prepared as previously described (5) except that 200 g. of tung oil, 64 g. of acrylonitrile, and 0.3 g. of hydroquinone were used. The product was not distilled, but after the excess acrylonitrile had been removed by vacuum-stripping on a steam cone with nitrogen as a sweep gas, the recovered adduct was filtered through a bed of Hyflo Super Cel. This material (224.3 g.) had: N, 2.8%; I.V. (hydrogenation), 119.7; sap. equiv., 315.3; $n^{20/D}$, 1.5013.

Hydrogenation of the Adducts. Similar procedures were applied during the hydrogenation of the four tung oil adducts described above. Two 40-g. samples of each adduct were hydrogenated at room temperature in a Parr hydrogenation apparatus with 3.0 g. of 10% palladium-carbon as a catalyst and 150 ml. of ethyl acetate as a solvent. The hydrogenation was initiated at about 40 lbs. pressure and continued until the rapid absorption of hydrogen ceased, indicating that the ethylenic bonds present in the addition products were saturated. In most cases this required 1 hr. The hydrogenated materials were filtered repeatedly through Hyflo Super Cel until free of the catalyst, vacuum-stripped on a steam cone with carbon dioxide as a sweep gas to remove the solvent, then filtered again through Hyflo Super Cel until clear. Analyses of the products showed that hydrogenation produced no significant changes in their saponification equivalents or in the carbonyl or nitrogen contents of the methyl vinyl ketone and acrylonitrile adducts. The hydrogenated adducts had these refractive indices, $n^{20/D}$: methyl vinyl ketone-tung oil, 1.4822; dimethyl maleate-tung oil, 1.4695; methyl acrylate-tung oil, 1.4665; acrylonitrile-tung oil, 1.4840.

Evaluation Procedures. The eight derivatives of tung oil were screened as Buna-N rubber softeners, using the following formulation:

Nitrile rubber (Hycar 1042—	
33% acrylonitrile).....	100.0
SRF Black.....	60.0
Zinc oxide.....	5.0
Stearic acid.....	1.5
Sulfur.....	1.5
Benzothiazyl disulfide.....	1.5
Softener.....	20.0
Cure: 30 min. at 310°F.	

Milling, curing, and testing procedures were the same as those reported elsewhere (7). The plasticizers were rated as compatible if formulations showed no signs of exudation or contact smearing within the observed 90 days of shelf aging.

Discussion

The results of the plasticizer screening tests for the hydrogenated and unhydrogenated tung oil adducts compounded with Buna-N rubber are presented in Table I. Milling of all of the eight experimental softeners appeared satisfactory. However the hydrogenated tung oil adducts of methyl vinyl ketone and of acrylonitrile became incompatible after shelf aging for periods of 14 and 21 days, respectively. The tung oil adducts of dimethyl maleate, methyl acrylate, and acrylonitrile, and the hydrogenated dimethyl maleate and methyl acrylate adducts yielded rubbers which met the low-temperature flexibility requirements ($-40^{\circ}\text{C}.$) of the automotive industry. The tung oil adducts before hydrogenation were superior to their hydrogenated counterparts and to the control, dibutyl sebacate, in plasticizing efficiency, *i.e.*, lower modulus, reduced hardness, and greater elongation. In all cases hydrogenation of the tung oil adducts resulted in a slight impairment of their plasticizing efficiency. Moreover the hydrogenated tung oil adducts of methyl vinyl ketone and of acrylonitrile caused severe impairment as seen by their early exudation from their molded stocks. Only the hydrogenated and unhydrogenated derivatives of dimethyl maleate and methyl acrylate yielded stocks that were comparable to the control in volume change. It was observed that all the compositions containing the adduct, when subjected to

accelerated aging tests, exhibited better modulus, elongation, and weight-loss properties than did the composition containing the control softener.

Summary

Eight derivatives of tung oil, namely, the methyl vinyl ketone, dimethyl maleate, methyl acrylate, and acrylonitrile adducts, and their hydrogenated products, were prepared and screened as softeners for Buna-N rubber with dibutyl sebacate as the control. Five of the eight products evaluated yielded stocks that met the low-temperature flexibility requirements ($-40^{\circ}\text{C}.$) of the automotive industry. In all cases the stocks prepared from the unhydrogenated derivatives were superior in plasticizing efficiency to the stocks prepared from their hydrogenated counterparts or to those prepared from the control.

Acknowledgments

The authors express their appreciation to Marian C. Willis and Alva F. Cucullu for their analytical assistance.

REFERENCES

1. Semon, W. L., in "Synthetic Rubber," edited by G. S. Whitby, C. C. Davis, and R. F. Dunbrook, pp. 794-837, John Wiley and Son Inc., New York, 1954.
2. Hoffmann, J. S., and Bickford, W. G., "New Tung Oil Derivatives," U. S. Dept. Agr., *ARS-72-7*, 1-16 (1956).
3. Hoffmann, J. S., O'Connor, R. T., Magne, F. C., and Bickford, W. G., *J. Am. Oil Chemists' Soc.*, **32**, 533-538 (1955).
4. Hoffmann, J. S., O'Connor, R. T., Magne, F. C., and Bickford, W. G., *J. Am. Oil Chemists' Soc.*, **33**, 410-414 (1956).
5. Placek, L. L., Mod, R. K., Magne, F. C., and Bickford, W. G., *J. Am. Oil Chemists' Soc.*, **35**, 584-586 (1958).
6. Placek, L. L., Magne, F. C., and Bickford, W. G., *J. Am. Oil Chemists' Soc.*, **36**, 651-652 (1959).
7. Fore, S. P., Pastor, H. P., Hughes, J. P., and Bickford, W. G., "Derivatives of Jojoba Oil as Plasticizers for Vinyl Polymers and Buna-N Rubber," *J. Am. Oil Chemists' Soc.*, in press.

[Received March 10, 1960]

ABSTRACTS . . . R. A. REINERS, Editor

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Sini'tiro Kawamura, F. A. Kummerow, Louise R. Morrow, and E. G. Perkins

• Fats and Oils

DIMORPHECOLIC ACID—A UNIQUE HYDROXYDIENOIC FATTY ACID. C. Smith, Jr., T. Wilson, E. Melvin, and I. Wolff (Northern Regional Res. Lab., Peoria, Illinois). *J. Am. Chem. Soc.* **82**, 1417-1421 (1960). Dimorphecolic acid, the chief constituent fatty acid of *Dimorphotheca aurantiaca* seed oil, is characterized as an optically active 9-hydroxy-*trans,trans*-10,12-octadecadienoic acid.

THE EPOXY ACIDS OF CHRYSANTHEMUM CORONARIUM AND CLARKIA ELEGANS SEED OILS. C. R. Smith, Jr., M. O. Bagby, R. L. Lohmar, C. A. Glass, and I. A. Wolff. *J. Organic Chem.* **25**, 218-22 (1960). Coronaric acid, the constituent epoxy acid of *Chrysanthemum coronarium* seed oil, is characterized as *cis*-9,10-epoxy-*cis*-12-octadecenoic acid. The epoxy acid of *Clarkia elegans* seed oil is identified as vernolic acid.

THEORETICAL PLATES IN GAS CHROMATOGRAPHY. EFFECTS OF DISTRIBUTION RATIO, VISCOSITY, AND AMOUNT OF LIQUID PHASE. J. J. Duffield and L. B. Rogers (Dept. of Chemistry, Massachusetts Institute of Technology, Cambridge 39, Mass.). *Anal. Chem.* **32**, 340-3 (1960). The value of the mass-transfer term in the van Deemter, Zuiderweg, and Klinkenberg equation increases with the viscosity and volume of the liquid phase. For distribution ratios greater than unity, the term is larger for the smaller ratios. With an increase in the mass-transfer term,

lower efficiencies are observed and adjustment of the flow rate for optimum conditions is critical. The optimum flow rate for inefficient columns is generally low; hence long times are necessary for analysis. Very small samples of vapor rather than liquid were used successfully and required no extrapolation to zero size.

RESPONSE OF THERMAL-CONDUCTIVITY CELLS IN GAS CHROMATOGRAPHY. L. J. Selmauch and R. A. Dinerstein (Research and Development Dept., Standard Oil Co., Whiting, Ind.). *Anal. Chem.* **32**, 343-52 (1960). To understand better the performance of thermal-conductivity cells as detectors in gas chromatography, theoretical and experimental studies were made of the response of cells to changes in gas composition and operating temperatures. An equation for response was derived for cells in which most of the heat is conducted through the gas. Response was considered as the product of two factors: one, a cell factor, depends on operating conditions including electrical parameters of the cell and bridge; and the other, a thermal-conductivity factor, depends on the difference in conductivity of the carrier gas and the gas mixture passing through the cell when a component is eluted.

COCONUT-LIKE FLAVOR DEFECT OF MILK FAT. IV. DEMONSTRATION OF δ -DODECALACTONE IN THE STEAM DISTILLATE FROM MILK FAT. B. W. Tharp and S. Patton (Dept. Dairy Science, Pennsylvania Agricultural Experiment Station, University Park).