Derivatives of Jojoba Oil as Plasticizers for Vinyl Polymers and Buna-N Rubber[1]

SARA P. FORE, H. P. PASTOR, J. P. HUGHES, and W. G. BICKFORD,
Southern Regional Research Laboratory,[2] New Orleans, Louisiana

JOJOBA OIL is unique among vegetable oils in that it reportedly contains no glycerides and is essentially a liquid wax composed principally of eicosenol, docosenol, eicosenoic acid, and docosenoic acid (1). It was reported in a prior publication that epoxidized jojoba oil imparted improved light and heat stability to vinyl chloride-containing plastics (2). In order to investigate further the applicability of jojoba derivatives to the plasticizer field, a number of maleinated derivatives of jojoba oil have been prepared and tested both as plasticizers for polyvinyl chloride-polyvinyl acetate copolymer and as softeners for nitrile rubber (Buna-N).

It has been established previously (3, 4) that maleinization of monoethenoid compounds results in the formation of alkenyl succinic anhydrides in which the anhydride moiety is attached to a carbon atom *alpha* to the double bond. It was assumed therefore that products of the same nature would result from the maleinization of jojoba oil or its components.

Experimental

Materials. Jojoba oil (I.V., 83.4; sap. equiv., 90.0) was obtained by cold pressing of jojoba nuts. Jojoba alcohols (I.V., 81.1; % OH, 5.4) were prepared by vacuum distillation of the ether-soluble fraction extracted from the saponified oil. The acids (I.V., 82.3; neut. equiv., 316.5) were obtained by vacuum distillation of the free fatty acids resulting from acidification of the alcohol-free soaps. Acetylated jojoba alcohols (I.V., 71.8; sap. equiv., 364.8) were prepared by the acetylation procedure described in A.O.C.S. method Cd 4-40 (5). All of the other reagents were of commercial origin and were used without further purification.

Maleinization Procedure. One double bond equivalent of the material to be maleinated was stirred with two moles of maleic anhydride at 200°C. until iodometric titration of an aliquot of the reaction mixture indicated that approximately one mole of maleic anhydride had been consumed. The reaction mixture was dissolved in benzene and washed with water for the removal of the major part of the unreacted maleic anhydride.

Esterification Procedure. The methyl esters were prepared by dissolving the adduct in 10 volumes of absolute methanol containing 2% of sulfuric acid and refluxing for 16 hrs. The reaction mixture was concentrated by distillation of methanol, after which it was diluted with water and the esters extracted with ethyl ether. The ethereal solution was washed first with 2% sodium hydroxide solution, then with distilled water, and was finally dried over anhydrous sodium sulfate. After removal of most of the ether by distillation, the sample was stripped with nitrogen gas at 60–90°C. under high vacuum.

The butyl esters were prepared by refluxing the adduct with an equal volume of toluene, which contained 3.0 g. of *p*-toluenesulfonic acid, and a 20% excess of *n*-butanol until the calculated quantity of water had been collected in a Dean-Stark trap. The reaction mixture was diluted with ether, and the *n*-butyl ester was recovered by the same procedure employed for the methyl ester. Methyl and butyl esters of the maleinated jojoba acids were distilled under high vacuum.

Hydrogenation Procedure. Approximately 30 g. of adduct were hydrogenated at room temperature in a Parr hydrogenation apparatus, using 150 ml. of ethanol as solvent and 3 g. of 10% palladium on carbon as catalyst. The hydrogenation was initiated at 30 lbs. of pressure and was continued until hydrogen uptake ceased, at which time the theoretical quantity of hydrogen had been absorbed. The reaction mixture was filtered to remove the catalyst, and the solvent was removed by vacuum stripping, employing nitrogen gas.

The materials prepared by the above procedures together with the iodine values of the unsaturated compounds are listed below. Iodine value, rather than saponification equivalent, was used as a criterion of purity as it is well recognized that saponification equivalents of alkenyl succinates cannot be determined accurately (6).

Methyl esters of maleinated jojoba oil (I.V., calcd., 58.6; found, 49.2)
Butyl esters of maleinated jojoba oil (I.V., calcd., 48.1; found, 38.5)
Methyl esters of maleinated jojoba acids (I.V., calcd., 54.2; found, 54.2)
Hydrogenated methyl esters of maleinated jojoba acids
Butyl esters of maleinated jojoba acids (I.V., calcd., 42.7; found, 43.0)
Hydrogenated butyl esters of maleinated jojoba acids
Methyl esters of maleinated acetylated jojoba alcohols (I.V., calcd., 50.9; found, 50.2)
Hydrogenated methyl esters of maleinated acetylated jojoba alcohols
Butyl esters of maleinated acetylated jojoba alcohols (I.V., calcd., 43.6; found, 45.0)
Hydrogenated butyl esters of maleinated acetylated jojoba alcohols

Evaluation Procedures. The ester preparations were evaluated as plasticizers in a copolymer vinyl composition (polyvinyl chloride-polyvinyl acetate) and as softeners in a nitrile rubber composition (butadiene-acrylonitrile).

The experimental plasticizers, which were incompatible or tested poorly as primary plasticizers, were blended (50-50) with di-2-ethylhexyl phthalate (con-

---

[1] Presented at the 51st annual meeting, American Oil Chemists' Society, Dallas, Tex., April 4–6, 1960.

[2] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

trol plasticizer) and evaluated as secondary plasticizers. The basic formula used was

Vinylite VYDR (95% polyvinyl chloride—5% polyvinyl acetate)	63.5%
Plasticizer	35.0%
Stearic acid	0.5%
Basic lead carbonate	1.0%

The plasticizer was added to a dry mixture of the other three components just prior to milling the stock on a 12 x 6-in. rubber mill at 310°F. The batch was added to a tight mill and permitted to form a sheet (2 min.). This sheet was continuously worked for 8 min., making ¾ cuts from one side and then from the other. The batch was sheeted off and permitted to cool; a small portion was removed for remilling into a thin sheet (9–11 mil.), which was employed for volatility and heat-stability tests. The remainder of the sheeted stock was molded in a standard 6 x 6 x 0.075-in., four-cavity mold. Since the thickness of the sheeted resin was much less than 0.075 in., several layers were placed in each mold with the milling axes parallel. Each 6 x 6 cavity mold was subjected to pressure, which was gradually increased over a period of 10 min. to a minimum of 500 p.s.i. and then held for an additional 10 min. at the molding temperature of 310°F. The pressure on the plasticized stocks was maintained until the molds were cool.

The procedures followed for determining tensile strength, ultimate elongation, and 100% modulus have been described previously (7). ASTM D 676-55T and D 746-44T test procedures were employed for the determination of hardness and brittle point, respectively. The procedure used for determination of volatility was essentially the same as that described in ASTM test D 1203-55 except that the thin specimens were equilibrated at 70°F. and 65 ± 2% relative humidity for at least 24 hrs. before and after oven-aging. For the determination of heat stability, thin 2½ x 4-in. specimens were heated in a forced draft oven at 176°C. for a total time of 2 hrs. The specimens were withdrawn at 30-min. intervals for determination of reflectance with a multipurpose reflectometer.[3] The relative compatibilities were judged by observing whether or not the molded slabs exuded or smeared on contact during shelf-aging for 225 days at room temperature.

The methyl and butyl esters of modified jojoba oils were screened as 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.

The milling and curing procedures were basically the same as those described in ASTM Test D 15-55T except that the stock was milled on the faster back roll (8) and that during the milling operation a dry mixture of zinc oxide, stearic acid, and sulfur was first added to the masticated rubber, followed by the alternate addition of small portions of SRF black and the softener. The unvulcanized stock was permitted to rest over-night (9) before the accelerator (benzothiazyl disulfide) was added to it on the milling rolls.

The cured samples of formulated rubber and all-rubber specimens subjected to heat treatment were conditioned for 24 hrs. at 70°F. and 65 ± 2% relative humidity before testing. Methods described in ASTM Test D 452-51T were used for determining tensile strength, elongation, and modulus on the specimens stamped out with cutting die D. The properties of hardness, brittle point, and compatibility were determined according to the same methods used for the copolymer-vinyl plastics. In the accelerated aging tests two dumb-bell specimens resting flat on a sheet of aluminum foil were placed in a forced draft oven for 48 hrs. at 212°F. Weighings for weight-loss determinations was made on accelerated aged samples before and after oven aging. The volume change procedure employed was that specified in Method A, ASTM Test D 471-55T, except for the following modifications: the immersion solvent consisted of a mixture of 70 volumes of iso-octane and 30 volumes of toluene; the dimensions of the test specimens were 1 x 1 x 0.075 in.

TABLE I

Properties of Vinyl Copolymer (VYDR) Plasticized with Jojoba Esters

Plasticizer	Tensile strength, p.s.i.	Ultimate elongation, %	100% Modulus, p.s.i.	Hardness shore A 10 sec.	Brittle point, °C.	Volatility wt. loss, %	Heat stability—% reflectance					Compatibility, days[a]
							Minutes heated					
							0	30	60	90	120	
Maleinatd acetylated jojoba alcohols												
Methyl esters + DOP (50-50)	3160	350	1990	47	−34	1.43	77.8	69.6	71.5	57.2	22.6	75[b]
Hydrogenated maleinated acetylated jojoba alcohols												
Methyl esters + DOP (50-50)	3120	340	1880	47	−34	1.38	78.9	73.7	75.1	59.9	29.5	7[b]
Maleinated jojoba oil												
Methyl esters	2890	280	1910	48	−30	0.72	75.6	55.1	52.5	49.0	23.5	21[b]
Methyl esters + DOP (50-50)	3190	360	1750	42	−30	1.25	78.2	69.4	73.3	30.0	21.6	225
Butyl esters + DOP (50-50)	3070	360	1830	47	−34	1.92	79.2	73.6	34.4	25.5	18.5	225
Maleinated jojoba acids												
Methyl esters	2810	280	1560	40	−30	0.91	78.5	71.5	59.6	21.5	18.1	225
Butyl esters	2460	210	1720	46	−42	0.98	77.9	65.5	43.3	22.5	18.4	225
Butyl esters + DOP (50-50)	3090	360	1610	44	−40	1.42	79.7	76.0	40.5	24.0	19.2	225
Hydrogenated maleinated jojoba acids												
Methyl esters	2810	290	1670	41	−32	1.08	75.3	56.5	50.3	32.7	14.0	225
Butyl esters + DOP (50-50)	3050	360	1630	43	−40	1.27	79.2	73.4	32.7	26.3	22.2	225
DOP (Di-2-ethylhexyl phthalate) control	2850	300	1590	42	−32	2.19	77.1	70.7	20.0	16.8	16.0	225

[a] Indicates no exudation during time specified. [b] Smears on contact.

---

[3] Amber 45°, 0° direction reflectance.

TABLE II

Properties of Nitrile Rubber (Hycar 1042) Plasticized with Jojoba Esters

Softener	Tensile strength p.s.i.		Ultimate elongation %		300% Modulus p.s.i.		Hardness shore A, 10 sec.	Weight loss, %	Brittle point, °C.	Volume change after 72 hrs. at 78°F., %	Compatibility days[a]
	Unaged	Aged[c]	Unaged	Aged[c]	Unaged	Aged[c]					
Maleinated acetylated jojoba alcohols											
Methyl esters	2320	2320	690	500	1030	1730	42	0.61	−40	23.9	225
Hydrogenated maleinated acetylated jojoba alcohols											
Methyl esters	2390	2190	660	460	1120	1780	43	0.57	−38	24.5	1[b]
Maleinated jojoba oil											
Methyl esters	2320	2270	680	480	1030	1720	43	0.63	−44	23.4	225
Maleinated jojoba acids											
Methyl esters	2430	2450	730	520	1020	1790	44	0.59	−46	21.5	225
Butyl esters	2380	2320	710	490	1040	1780	42	0.54	−56	22.7	225
Hydrogenated maleinated jojoba acids											
Methyl esters	2340	2290	660	480	1110	1740	44	0.63	−48	20.8	225
Butyl esters	2300	2330	640	550	1110	1780	44	0.49	−56	24.2	225
DBS (dibutyl sebacate) control	2160	2380	630	480	1090	1990	44	5.48	−52	20.0	225

[a] *Indicates no exudation during time specified.* [b] Develops tacky surface 24 hrs. after milling. [c] Aged in air oven at 212°F. for 48 hrs.

Results and Discussion

Evaluation of Esters in Vinyl Copolymer. The results of the plasticizer screening tests for all of the jojoba esters which were compatible on the milling rolls as either primary or secondary plasticizers are presented in Table I. On examining the data, it is observed that methyl esters were superior to butyl esters with respect to compatibility on the milling rolls and in plasticizing efficiency as exhibited by lower modulus, reduced hardness, and greater elongation. Only in low-temperature-flexibility properties do the butyl esters excel the methyl esters. This is shown by a comparison of the data for the methyl and the butyl esters, both in the straight maleinated jojoba acids and in the blends of DOP and maleinated jojoba oil.

Hydrogenated and unhydrogenated maleinated acetylated jojoba alcohols exhibited the poorest qualities of all the modified esters tested. The butyl esters of this series also were prepared, but no data are tabulated for them since they could not be milled in the formulation. Of the three experimental plasticizers that showed acceptable characteristics as primary plasticizers, two preparations, the methyl esters of hydrogenated and of unhydrogenated maleinated jojoba acids, were comparable to the control (DOP) in plasticizing efficiency and brittle point. The corresponding butyl esters of maleinated jojoba acids, although deficient in plasticizing efficiency, showed better low-temperature properties than the DOP control (−42°C. brittle point compared to −32°C.).

The volatility and heat-stability tests indicated that jojoba esters, blended or unblended, had greater permanence in the vinyl resin than did the DOP control. Hydrogenation resulted in a slight impairment of the plasticizing properties of the methyl esters of maleinated jojoba acids. However, in the case of the corresponding butyl esters, severe impairment resulted to the point of rendering them incompatible in the milling operation. The use of the butyl esters of both hydrogenated and unhydrogenated maleinated jojoba acids as secondary plasticizers in combination with DOP (50-50 blend) produced vinyl compositions of better over-all qualities than the control. In low-temperature, brittle point particularly, the blends (brittle point −40°C. for each) excelled.

Evaluation as Softeners for Buna-N Rubber. Table II presents the results of evaluations as softeners in a Buna-N rubber formulation of the several jojoba oil derivatives. Similarity between the vinyl copolymers and the nitrile rubber studies is shown by the failure of the butyl esters of the acetylated jojoba alcohol series to mill into the formulation. For this reason no data for these materials are presented. Additional evidence of incompatibility in the formulation was exhibited by the butyl esters of maleinated jojoba oil, which exuded excessively within 24 hrs. after milling. Of the eight derivatives which milled satisfactorily, only the methyl ester of hydrogenated maleinated acetylated jojoba alcohols and the butyl ester of maleinated jojoba oil later became incompatible. The latter material exuded excessively 24 hrs. after milling, thus preventing its evaluation. The other six softeners are equivalent or superior to the control softener, dibutyl sebacate, in all properties tested. With respect to permanence the experimental products were comparable to the control formulation in volume change but were vastly superior in weight loss and modulus after aging. The compatible softener preparations excelled the control, DBS, in plasticizing efficiency (lower modulus, reduced hardness, and greater elongation) except for the hydrogenated maleinated jojoba acid series which are, in general, comparable to the control. The butyl esters of both hydrogenated and unhydrogenated maleinated jojoba acids are outstanding among the jojoba derivatives tested in their low-temperature characteristics and also compare favorably with the control, DOP, in this respect.

Summary

Ten maleinated jojoba oil derivatives were screened as plasticizers in a standard polyvinyl resin formulation and as softeners for Buna-N rubber. Three of these, the methyl and butyl esters and hydrogenated methyl esters of maleinated jojoba acids, were comparable to the reference standard, DOP, as primary plasticizers for the vinyl resin. Three others were satisfactory only as secondary plasticizers. Six of the derivatives were comparable to the reference softener, dibutyl sebacate, as softeners in a Buna-N formulation and yielded rubbers meeting the low temperature flexibility requirements (−40°C.) of the automotive

industry. Two of the six, those made with the butyl and hydrogenated butyl esters of maleinated jojoba acids, met the still more stringent low-temperature requirements of the aircraft industry (−55°C.).

In general, hydrogenation of a derivative adversely affected its compatibility in either the vinyl copolymer or the Buna-N formulations.

Acknowledgments

The authors wish to acknowledge the assistance of Vidabelle O. Cirino, Alva F. Cucullu, Voyce P. Whitley, and Marian C. Willis in conducting the analyses of the derivatives.

REFERENCES

1. Daugherty, P. M., Sineath, H. H., and Wastler, T. A., Georgia Inst. Technol., State Eng. Expt. Sta. Bull., *No. 17*, 36 pp. (1953).
2. Fore, Sara, P., Magne, F. C., and Bickford, W. G., J. Am. Oil Chemists' Soc., *35*, 469–472 (1958).
3. Bickford, W. G., Krauczunas, P., and Wheeler, D. H., Oil and Soap, *19*, 23–27 (1942).
4. Bickford, W. G., Fisher, G. S., Kyame, L., and Swift, C. E., J. Am. Oil Chemists' Soc., *25*, 254–257 (1948).
5. American Oil Chemists' Society, "Official and Tentative Methods of Analysis," 2nd ed., rev. to 1958, V. C. Mehlenbacher and T. H. Hopper, eds., Chicago, 1946–1958.
6. Danzig., M. J., O'Donnell, J. L., Bell, E. W., Cowan, J. C., and Teeter, H. M., J. Am. Oil Chemists' Soc., *34*, 136–138 (1957).
7. Magne, F. C., and Mod, R. R., Ind. Eng. Chem., *45*, 1546–1547 (1953).
8. Semon, W. L., in "Synthetic Rubber," edited by G. S. Whitby, C. C. Davis, and R. F. Dunbrook, p. 794–831, John Wiley and Son Inc., New York, 1954.
9. Klebsattel, C. A., India Rubber World, *102*, No. 5, 33–35 (1940).

[Received February 8, 1960]

Relative Esterifiability of the Primary and Secondary Hydroxyl Groups of Glycerol[1]

J. D. BRANDNER and R. L. BIRKMEIER, Atlas Powder Company, Wilmington, Delaware

MONOGLYCERIDES are made commercially either by the esterification of fatty acids with glycerol or by the alcoholysis of a fat with glycerol. The product is a mixture of mono-, di-, and triglycerides with unreacted glycerol. The last is frequently removed at the end of the reaction period.

Feuge and Bailey (5) recognized that since monoglycerides are customarily prepared at high temperatures in the presence of alkaline catalysts, conditions exist which are favorable to ester interchange equilibrium. They showed that the proportions of glycerol, mono-, di-, and triglycerides can be calculated statistically if one makes the following two assumptions: a) that there is a random distribution of acyl groups on the hydroxyls of glycerol and b) that there is equal probability that the primary and secondary hydroxyl groups will be esterified. According to Feuge and Bailey, the predicted and experimentally estimated compositions were in reasonably good agreement. Although the method of calculation presented by them has contributed greatly to elucidating the composition of commercial monoglycerides, there appears to be an inconsistency in their comparison of experimental and calculated compositions. In a recent review of the literature on monoglycerides Demarcq (4) noted the following: "Feuge and Bailey appear to rely on two contradictory postulates: that of equal chance of esterification of hydroxyls on the one hand and that of the nonformation of *beta* monoglyceride on the other hand." Demarcq attempted unsuccessfully to devise a method of estimating relative hydroxyl reactivity. The work reported here was directed at re-examining the assumptions required to predict the distribution of acyl groups.

The first assumption necessary to predict the equilibrium composition of mixed partial esters of any polyol is that the chance that any hydroxyl will be esterified is determined by the relative molar proportions of acyl groups to hydroxyl groups. It is further implied that the presence of one acyl group on a polyol is without effect on the esterifiability of the remaining hydroxyl groups. In order to test this assumption, the equilibrium composition of the reaction product of oleic acid and ethylene glycol was determined. Ethylene glycol (Carbide and Carbon) was reacted in approximately equimolar proportions with commercial oleic acid (Emersol 233LL, Emery Industries) at 175°C. under nitrogen, using 0.1% NaOH as catalyst. The contents of the flask were sampled after approximately 1¾, 5¼, and 12¼ hrs and analyzed for acid number and saponification number by essentially the A.O.C.S. methods; for hydroxyl number by a modification of the method of West, Hoagland, and Curtis (11); and for free ethylene glycol by periodate consumption. Results of the analyses are given below:

Time—hours	1¾	5¼	12¼
Acid number	42.1	5.3	2.4
Saponification number	177.5	178.0	178.5
Hydroxyl number	181.0	155.0	142.5
Weight % free glycol	5.9	3.8	3.6

The ester number and hydroxyl number of the ester portion can be calculated on a free glycol- and fatty acid-free basis by using 276 as the molecular weight of the acid as determined from its acid number. As has been shown elsewhere (1), the mole ratio of monoester to diester, M, can be computed from the relation

$$M = \frac{2}{(E/H) - 1}$$

where E and H are the ester number and hydroxyl number, respectively, of the ester portion. The weight ratio of monoester to diester is equal to 320M/578, where 320 and 578 are the average molecular weights of ethylene glycol mono- and diesters of commercial oleic acid, respectively. From the weight percentage of free glycol, monoester, and diester in the acid-free product, the mole fractions can be computed very simply with the results given below:

---

[1] Presented at the 50th annual meeting, American Oil Chemists' Society, New Orleans, La., April 20–22, 1959.