Amide Plasticizers From Safflower and Tall Oil Derived Fatty Acids

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ABSTRACT

Fatty acids derived from a high oleic strain of safflower seeds are eminently suited for the preparation of compatible and efficient N,N-disubstituted fatty acid amide polyvinyl chloride plasticizers with low temperature properties in the adipate-azelate range. N,N-disubstituted amides of tall oil-derived acids, Westvaco Type 1480, give comparable plasticizing performance. Polyvinyl chloride compositions plasticized with the hexachlorocyclopentadiene adduct of N,N-dibutyloleamide show no soapy water extraction loss.

INTRODUCTION

It has been established that many N,N-disubstituted amides of selected long chain fatty acids and fatty acid mixtures (1-8) are effective plasticizers for homo- and copolymers of vinyl chloride. Of these, the N,N-dialkylamides of oleic and oleic-rich fatty acid mixtures perform best and are, in addition, the most promising economically.

To broaden the spectrum of operable fatty acids we have recently investigated the applicability of a commercial, predominately monoolefinic, C_{18} fatty acid high in *trans*-isomers, as well as the crude and refined fatty acid mixtures derived from a high oleic strain of safflower seeds (9) as raw materials for amide plasticizers. The utility of N-methylethanolamine as a precursor of operable oleic acid ester-amide plasticizers or extenders was also investigated for precisely the same reason.

This report covers the plasticizing characteristics of the N,N-dimethyl and N,N-dibutylamides of the forementioned acid mixtures, and that of N,N-dibutyloleamide (DBO) at various levels of incorporation with polyvinyl chloride, as well as that of N-methyl-N-(2-oleoyloxyethyl)oleamide and its blends with DBO or di-2-ethylhexyl phthalate (DOP).

EXPERIMENTAL PROCEDURES

Westvaco 1480 is a commercial tall oil product of the West Virginia Pulp and Paper Company and is a predomin-

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TABLE I

Plasticizing Characteristics of N,N-Dimethyl and N,N-Dibutyl Amides of Safflower and Tall Oil Oleic Type Acids and an Ester Amide With Polyvinyl Chloride

Plasticizer	Per Cent	Resin	Tensile strength, psi	100% Modulus, psi	Elongation, %	Brittle point, C	Volatility loss, %	Compatibility[a]
1. Dimethylamide crude safflower oil acids	35	Geon 101	2630	1290	330	-59	5.2	C
2. Dimethylamides refined safflower oil acids	35	Geon 101	2640	1250	330	-50	4.2	C
3. Dibutylamide crude safflower oil acids	35	Geon 101	2390	1550	230	-53	2.5	C
4. Dibutylamide refined safflower oil acids	35	Geon 101	2480	1610	250	-55	1.0	C
5. Dimethylamide westvaco oleic acid	35	VYNW-5	2620	1320	345	-38[b]	-----	C
6. Dibutylamide westvaco oleic acid	35	VYNW-5	2610	1540	280	-51	-----	C
7. HCPD adduct of N,N-dibutyloleamide[c]	35	VYNW-5	3380	3140	260	+ 3	<0.1	C
8. N-Ethoxyethyloleamide	35	VYNW-5	← (Incompatible	at room	temperature) →			I
9. N-Methyl-N-(2-oleoyloxyethyl) oleamide	35	VYNW-5	2470	1710	280	-47	1.9	I
10. 75% #9 + 25% DOP[d]	35	Geon 101	2250	1820	160	-35	0.8	I
11. 50% #9 + 50% DOP	35	Geon 101	2890	1870	315	-37	0.7	C
12. 25% #9 + 75% DOP	35	Geon 101	3020	1820	330	-33	1.0	C
13. 75% #9 + 25% DBO[e]	35	Geon 101	2180	1710	180	-37	0.6	I
14. 50% #9 + 50% DBO	35	Geon 101	2450	1600	270	-44	0.6	C
15. 25% #9 + 75% DBO	35	Geon 101	2620	1490	320	-49	0.6	C
16. DBO	25	Geon 101	3510	2700	220	-28	-----	C
17. DBO	30	Geon 101	2940	1880	270	-38	-----	C
18. DBO	35	Geon 101	2640	1520	300	-59	1.1	C
19. DBO	40	Geon 101	2210	1010	400	-68	-----	C
20. Butyl 2-oleoyloxypropionate	35	Geon 101	2380	1800	150	-24	-----	I
DOP	35	Geon 101	3080	1730	330	-30	1.0	C
Di-2-ethylhexyl azelate	35	Geon 101	2410	990	390	-57	1.3	C

[a]C, compatible; I, incompatible.
[b]Tf value.
[c]HCPD, Hexachlorocyclopentadiene; Adduct, N,N-Dibutyl-8-(1,4,5,6,7,-7-hexachloro-3-octylbicyclo [2.2.1]-5-heptene-2yl)octanamide.
[d]DOP, Di-2-ethylhexyl phthalate.
[e]DBO, N,N-Dibutyloleamide.

ately monoolefinic C_{18} fatty acid mixture, high in *trans*-isomers. The safflower oil fatty acids were derived from the oil of a high oleic strain of safflower seeds. The dimethyl, dibutyl and N-methylethanol amines used were all commercial products. The N,N-dimethyl and N,N-dibutylamides of the safflower oil acids were prepared by reacting equimolar proportions of the acid chloride of the fatty acids and the respective amines. N-Methyl-N-(2-oleoylethyl)oleamide was prepared by refluxing two moles of oleic acid, Emersol 233LL, and one mole of N-methylethanolamine in the presence of benzene to azeotropically remove the water of reaction following the procedure already reported (10). The preparation of N,N-dibutyloleamide (5) and the hexachlorocyclopentadiene adduct of N,N-dibutyloleamide (11) have already been reported.

Plasticizer Screening

The amides were screened as plasticizers for polyvinyl chloride (Geon 101) or poly(vinyl chloride-vinyl acetate) copolymer (VYNW-5) using the following formulation: 63.5% polymer, 35% plasticizer, 0.5% stearic acid and 1.0% basic lead carbonate. When higher or lower plasticizer concentrations were employed the resin-plasticizer proportions were varied in accordance to the relation per cent resin = 98.5-α, where α is the percentage of plasticizer employed. The milling, molding and testing procedures were the same as previously reported (1) except for the use of 10-15 mil sheets in the volatility and soapy water extraction tests.

RESULTS AND DISCUSSION

The data, Table I, show that the safflower acids from both refined and crude oil, and the Westvaco 1480 acid are suitable sources for preparing N,N-dimethyl and N,N-dibutylamides compatible with the PVC polymer. Low temperature performance favors the safflower derivatives slightly, but there is little or no choice between the three respective acid mixtures on the basis of the other plasticizing properties imparted by the derived amides.

N-Methyl-N-(2-oleoyloxyethyl)oleamide is not suitable as either the sole plasticizer (Sample 9) or as an extender in blends with DOP or DBO which incorporate somewhat more than 50% of the extender (Samples 10 and 13) because of a compatibility deficiency. As would be expected, the compatible blends with DBO offer better efficiencies and low temperature performance than similar blends with DOP. Best tensile strength is imparted by the DOP blends. Volatility losses are just about the same for similar compositions in both blended series but only the compositions employing the DBO blends are antistatic. The hexachlorocyclopentadiene adduct of DBO, Sample 7, is noteworthy as an amide plasticizer for two reasons: its low volatility loss and more particularly its nonextractibility by soapy water. The latter is in sharp contrast to the 20% extraction loss found for a similar composition plasticized with unadducted DBO. HCPD thus provides a means of reducing the typically high soapy water extractability of the N,N-dibutyl and N,N-dimethylamides of C_{18} individual and mixed fatty acids.

Samples 8, N-ethoxyethyloleamide, and 20, butyl 2-oleoyloxypropionate, are oleic acid derivatives which were screened as PVC plasticizers in the course of this work, and, as shown in Table I, proved to be incompatible.

The performance of DBO as a plasticizer at various levels of incorporation with Geon 101 is shown in Table I, Samples 16 to 19. These data show that DBO is comparable to di-2-ethylhexyl azelate in low temperature performance and volatility loss, but not quite as efficient at the same levels of incorporation.

Both the safflower and Westvaco acids are suitable sources of fatty acid materials for preparing good performing N,N-disubstituted amide plasticizers. The N,N-dibutylamides are to be preferred for reasons of better low temperature and volatility characteristics. As stated previously, N-methyl-N-2-oleoyloxyethyloleamide is only suitable as an additive and cannot be used as the sole plasticizer in a PVC composition. The HCPD adduct is a specialty purpose or additive plasticizer.

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