The absence of monobasic acids other than nonanoic acid in the oxidative cleavage products shows that the hydroxyl groups are located on carbons 9 and 10 from the methyl end of each acid. Percentages of the four dibasic acids in the oxidation mixture have been interpreted as representing the composition of the original diol mixture. These values agree with the composition of the monoene mixture obtained from the diols by the Ames-Bowman procedure (2).

The conclusion that the vicinal dihydroxy acids of *Cardamine* oil have the *erythro* configuration is based on the observation that they are converted almost exclusively to *cis*-olefins by the procedure of Ames and Bowman (2). This procedure involves replacement of both hydroxyls with bromines by hydrogen bromide in acetic acid, and subsequent debromination with zinc. It is assumed that the bromination step inverts the configuration of one of the hydroxyl-bearing carbons, but not the other (16,17). *trans*-Elimination of the bromines by an E2-type mechanism is then effected by zinc. The net result is transformation of an *erythro*-diol to a *cis*-olefin. A small amount of isolated *trans*-unsaturation in these monoenes may indicate that some *threo*-diol is present in the mixture or that the conversion of diol to olefin is not completely stereospecific.

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[Received May 21, 1965—Accepted June 14, 1965]

N,N-Dialkylamides of Long Chain Fatty Acids as Plasticizers [1]

R. R. MOD, F. C. MAGNE and E. L. SKAU, Southern Regional Research Laboratory,[2] New Orleans, Louisiana

Abstract

A number of N,N-dialkylamides have been prepared, characterized and evaluated as plasticizers for poly(vinyl chloride-vinyl acetate) copolymer. Among these are the N-oleoyl derivatives of diisopropyl, dibutyl, diisobutyl, diamyl, dihexyl, diheptyl, dioctyl, di-2-ethylhexyl and didecylamines. Also included are the N,N-dibutylamides of 2-ethylhexanoic, neodecanoic, neotridecanoic, palmitic, stearic, linoleic, erucic, ricinoleic, naphthenic, dimer, pinic, epoxystearic, animal, cottonseed, hydrogenated cottonseed, rapeseed, *Limnanthes douglasii* seed and parsley seed acids. Optimum low-temperature plasticizing properties are achieved for the N-oleoyl derivatives of dibutyl, diamyl and dihexyl amines. These low-temperature properties are comparable to those of the adipate and sebacate plasticizers without the adverse volatility characteristics of the adipates. Compatibility of the N,N-dialkyloleamides extends through the dihexyl derivative. A brief heat stability study of some selected plasticized polylvinyl chloride copolymer compositions indicates that the thermal stabilization of amide plasticizers is not an insurmountable problem.

Introduction

IT HAS BEEN SHOWN in previous publications that many N,N-disubstituted long chain fatty acid amides such as the morpholides (1), N,N-bis(2-acyloxyethyl)amides (2), piperidides (3) and N,N-bis-(2-alkoxyethyl)amides (4), are acceptable primary plasticizers for polyvinyl chloride resins (PVC). Recent work has shown that still another type, the dialkylamides, characterized by excellent sebacate-like low-temperature performance, must be added to the group. This report deals with the preparation, characterization and plasticizer evaluation of a number of N-fatty acyl derivatives of various C_3 to C_{10} symmetrical dialkylamines and also includes a brief heat stability study of selected plasticized PVC compositions.

Experimental

The oleic acid (Emersol 233LL Elaine) and dimer acid (Empol 1014) were products of Emery Industries. Oleoyl chloride was prepared from the oleic acid. Neodecanoyl and neotridecanoyl chloride were obtained from Euron Laboratories. The "animal acids" mixture was an Armour & Co. product, Neofat 65, having the following compositional specifications: 2% myristic, 26% palmitic, 16% stearic, 48% oleic and 8% linoleic acids. Hydrogenated cottonseed acids were derived from a selectively hydrogenated oil (5) which had an iodine value of 73.0 and a thiocyanogen value of 68.0. Rapeseed, cottonseed, *Limnanthes douglasii* seed and parsley seed fatty acids were obtained by saponification of the respective oils. Ethyl-2,2-dimethyl-3-chlorocarbonyl-cyclobutaneacetate, used in the preparation of the pinic acid derivative, was furnished by the Naval Stores Laboratory of this Division. Linoleic acid, 95% purity, was obtained from the Northern Regional Research Laboratory. Di-*n*-hexylamine was a Sapon Laboratories product. All the other dialkylamines and acids were Eastman Kodak Co. products, "white label" when available. The naphthenic acid had a neutralization equivalent of 217.

TABLE I

Analyses and Physical Properties of N-Acyl Derivatives of Various Dialkylamines

N,N-Dialkylamides	Density 30C	n_D^{30}	% C		% H		% N	
			Exp.	Theory	Exp.	Theory	Exp.	Theory
N,N-Diisopropyloleamide	0.8376	1.4656	76.87	78.76	12.69	12.96	3.56	3.83
N,N-Diisobutyloleamide	0.8614	1.4620	78.78	79.24	13.10	13.06	3.56	3.56
N,N-Dibutyloleamide	0.8621	1.4620	78.85	79.24	12.94	13.05	3.44	3.56
N,N-Diamyloleamide	0.8587	1.4627	79.68	79.81	13.28	13.15	3.29	3.32
N,N-Dihexyloleamide	0.8558	1.4622	80.11	80.09	13.45	13.23	3.15	3.12
N,N-Diheptyloleamide	0.8546	1.4611	80.03	80.36	13.34	12.45	2.86	2.93
N,N-Dioctyloleamide	0.8563	1.4627	80.58	80.65	13.39	13.35	2.72	2.77
N,N-Di-2-ethylhexyloleamide	0.8670	1.4648	79.80	80.65	13.25	13.24	2.90	2.77
N,N-Didecyloleamide	0.8557	1.4653	81.01	81.13	13.37	13.45	2.43	2.49
N,N-Dibutyl-2-ethylhexanamide	0.8549	1.4462	74.97	75.16	12.84	12.92	5.15	5.48
N,N-Dibutylneodecanamide	0.8646	1.4532	76.10	76.19	13.25	13.05	4.90	4.94
N,N-Dibutylneotridecanamide	0.8696	1.4564	77.27	77.47	13.26	13.22	4.29	4.31
N,N-Dibutylpalmitamide	0.8525	1.4586	78.75	78.33	13.72	13.43	4.04	3.81
N,N-Dibutylstearamide	0.8519	1.4555	78.86	78.85	13.51	13.50	3.49	3.54
N,N-Dibutyllinoleamide	0.8703	1.4697	79.65	79.19	12.61	12.71	3.45	3.58
N,N-Dibutylerucamide	0.8594	1.4636	79.99	80.03	13.11	13.22	3.07	3.09
N,N-Dibutylricinoleamide	0.9016	1.4703	76.32	76.15	12.62	12.45	3.34	3.42
N,N-Dibutylnaphthenamide	0.9023	1.4715					4.20	4.27
N,N,N',N'-Tetrabutylamide of dimer acid	0.9010	1.4802					3.54	3.58
Ethyl 2,2-dimethyl-3-(dibutylamino)-carbonylcyclobutaneacetate	0.9554	1.4618	70.11	70.09	10.90	11.15	4.14	4.30
N,N-Dibutylepoxystearamide [a]								
N,N-Dibutylamide of animal acids	0.8614	1.4584					3.27	3.63
N,N-Dibutylamide of cottonseed oil fatty acids	0.8711	1.4650					3.26	3.65
N,N-Dibutylamide of hydrogenated cottonseed oil fatty acids	0.8601	1.4645					3.63	3.62
N,N-Dibutylamide of rapeseed oil fatty acids	0.8652	1.4641					3.08	3.37
N,N-Dibutylamide of Limnanthes douglasii oil fatty acids	0.8593	1.4632					3.23	3.25
N,N-Dibutylamide of parsley seed oil fatty acids	0.8871	1.4675					3.08	3.26

[a] Oxirane content 3.43, theory 3.73.

Unless otherwise mentioned all of the amides were prepared by the general procedure previously described (5) or by interaction of equimolar quantities of acid chloride and amine in the presence of pyridine. The N,N-dibutylricinoleamide was prepared from the methyl ester as described by Dupuy et al. (6). The N,N-dibutylepoxystearamide was prepared from N,N-dibutyloleamide by epoxidation with m-chloroperbenzoic acid. All these amides were completely freed of residual fatty acids by percolation of a hexane solution through activated alumina.

Densities were determined pycnometrically in a thermostated bath controlled to within 0.1C and refractive indices were measured at 30.0 ± 0.1C with a precision Bausch and Lomb refractometer.

Plasticizer Screening

These amides were all screened as plasticizers for 95% polyvinyl chloride—5% polyvinyl acetate copolymer and compared with di-2-ethylhexphthalate (DOP), dioctyl adipate (DOA), and dioctyl sebacate (DOS) as controls. The N,N-dibutyloleamide was also tested in the polyvinyl chloride homopolymer (Geon 101). The compounding formulation used was as follows: 63.5% resin, 35% plasticizer, 0.5% stearic acid and 1.0% basic lead carbonate. The milling, molding and testing procedures were the same as previously reported (1,7), except that 10–15 mil sheets were used in the volatility and thermal stability tests. Thermal stabilities were established in terms of the relative reflectances of the plasticized stock after subjection to increasing exposure periods in a forced draft oven maintained at 176C. These values were determined by means of a "Photoelectric Reflection Meter Model 610," using the amber 0°, 45° directional reflectance. Compositions which showed no signs of exudation during 90 days of shelf-storage were rated compatible.

Results and Discussion

The densities, refractive indices, and elemental analyses of the various fatty amides are tabulated in Table I.

The plasticizer evaluation data (Table II) show how the plasticizer performance in Vinylite VYDR is influenced on the one hand, by the length of the alkyl group attached to the nitrogen and on the other, by changes in the fatty acid moiety.

It is apparent from the performance of Samples 1 to 9 that both favorable and unfavorable effects are associated with the change in the N-alkyl groups. As the chain length increases up to a limiting number of six carbons both low-temperature performance and volatility loss show improvement; beyond this point a further increase has a recessive effect. Tensile strength, on the other hand, becomes slightly poorer with increasing chain length. Borderline compatibility was observed at the C_7 level and the C_8 derivative, N,N-dioctyloleamide, was grossly incompatible. The best overall balance in plasticizing properties is attained in the C_4 to C_6 chain length range, with a more favorable volatility picture at the upper end and a slightly more favorable tensile strength and modulus at the lower end of the range, there being but little change in low-temperature performance, which is at or close to the optimum. Comparison of Samples 2 and 3 indicate that branched N-alkyl substituents are inferior to their straight chain counterparts in their contribution to overall plasticizer performance.

The data for the dibutyl amides of various acids, Samples 3 and 10–27 in Table II show that the best overall plasticizing properties were exhibited by the oleic acid derivative, i.e., N,N-dibutyloleamide. Although certain specific characteristics such as volatility may improve at a higher level, as in the erucoyl (C_{22}) derivative, other characteristics such as brittle

TABLE II
Physical Characteristics of Vinyl Chloride-Vinyl Acetate Copolymer Stocks Plasticized with N-Acyl
Derivatives of Dialkylamines
(35% Plasticizer)

Sample number	Plasticizer	Tensile strength psi	100% Modulus psi	Elongation %	Brittle point °C	Volatility loss %	Compatibility [a]
1.	N,N-Diisopropyloleamide	2960	1660	360	−53	2.49	C
2.	N,N-Diisobutyloleamide	2730	1540	310	−55	2.64	C
3.	N,N-Dibutyloleamide	2710	1460	340	−63	1.27	C
3a.	N,N-Dibutyloleamide [b]	2640	1520	300	−59	1.07	C
4.	N,N-Diamyloleamide	2680	1500	330	−61	0.67	C
5.	N,N-Dihexyloleamide	2510	1630	280	−63	0.53	C
6.	N,N-Diheptyloleamide	1460	.... [c]	120	−33	0.84	B
7.	N,N-Dioctyloleamide			would not mill			I
8.	N,N-Di-2-ethylhexyloleamide			would not mill			I
9.	N,N-Didecyloleamide			would not mill			I
10.	N,N-Dibutyl-2-ethylhexanamide	2610	1180	350	−41	10.21	C
11.	N,N-Dibutylneodecanamide	2980	1570	340	−27	10.36	C
12.	N,N-Dibutylneotridecanamide	2970	2100	330	−23	9.66	C
13.	N,N-Dibutylpalmitamide	2730	1360	350	−47	0.66	C
14.	N,N-Dibutylstearamide	2540	1540	340	−37	0.93	I
15.	N,N-Dibutyllinoleamide	2760	1340	350	−57	2.23	I
16.	N,N-Dibutylerucamide	2380	1620	250	−57	0.28	C
17.	N,N-Dibutylricinoleamide			Immediate bleeding			I
18.	N,N-Dibutylnaphthenamide	2970	1610	300	−21	8.32	C
19.	N,N,N',N'-Tetrabutylamide of dimer acid	2950	2180	230	−23	0.00	C
20.	Ethyl 2,2-dimethyl-3-(dibutylamino)-carbonylcyclobutaneacetate	3060	1460	300	−7	5.16	C
21.	N,N-Dibutylepoxystearamide	2800	1190	360	−35	0.46	C
22.	N,N-Dibutylamide of animal acids	2600	1470	330	−51	0.62	C
23.	N,N-Dibutylamide of cottonseed oil fatty acids	2840	1310	400	−57	2.38	I
24.	N,N-Dibutylamide of hydrogenated cottonseed oil fatty acids	2630	1420	350	−57	1.11	C
25.	N,N-Dibutylamide of rapeseed oil fatty acids	2740	1650	290	−57	0.39	I
26.	N,N-Dibutylamide of *Limnanthes douglasii* oil fatty acids	2560	1520	330	−53	0.91	C
27.	N,N-Dibutylamide of parsley seed oil fatty acids	2810	1450	350	−57	2.16	C
	Di-2-ethylhexylphthalate (control)	3050	1610	330	−33	1.50	C
	Dioctyl adipate (control)	2890	1290	380	−55	6.0	C
	Dioctyl sebacate (control)	2690	1370	350	−59	0.59	C

[a] C = compatible; B = borderline; I = incompatible.
[b] Polyvinyl chloride (Geon 101).
[c] Elongation too rapid for measurement.

point, tensile strength and elongation, are adversely affected. Conversely, shortening the chain of the acyl moiety of the compatible saturated amides has a detrimental effect on volatility loss. The trends on the effect of branching on plasticizer performance parallel those previously noticed in diester plasticizers (8–10). The response to acyl branching is less clear in this series, Samples 10–13, because of superimposed molecular weight effects. However there is little doubt that double as opposed to single branching, Samples 11 and 12 vs. 10, particularily the alpha-alpha type, adversely affects the low-temperature performance and volatility loss characteristics of the plasticizer irrespective of any superimposed molecular weight effects. The diamide or ester-amide of dicarboxylic acids are, as usual, poorer performing plasticizers than monodialkylamides. The dimer acid derivative would be attractive when extremely low volatility characteristics are a prime consideration. This has been a general observation (3,4) regardless of the N,N-substituent.

The N,N-dialkylamides at the optimum performance level of acyl and N-alkyl moieties, i.e., the N-n-dibutyl through N-n-dihexyloleamides, having brittle points of −61C to −63C, are definitely comparable to dioctyl sebacate and dioctyl adipate in low-temperature performance, and markedly superior to dioctyl adipate in volatility-loss characteristics. The sebacate-like low-temperature performance of the N,N-dibutyloleamide is confirmed by the identical contours of the stiffness-temperature curves (Figure 1) of the N,N-dibutyloleamide and dioctyl sebacate-plasticized compositions. Obviously both compositions must exhibit the same T_f and T_4 values of −58 and −17C, respectively. The gradual rate of change in the stiffness-temperature relation is most desirable.

Soapy water extractibility, 20.5%, is rather high compared to that of these diester controls but about average for amides.

Oleic acid is the only naturally occurring C_{18} fatty acid investigated which gives a compatible N,N-dibutyl amide. The amides derived from naturally occurring fatty acid mixtures such as cottonseed and rapeseed acids (samples 23 and 25), which contain
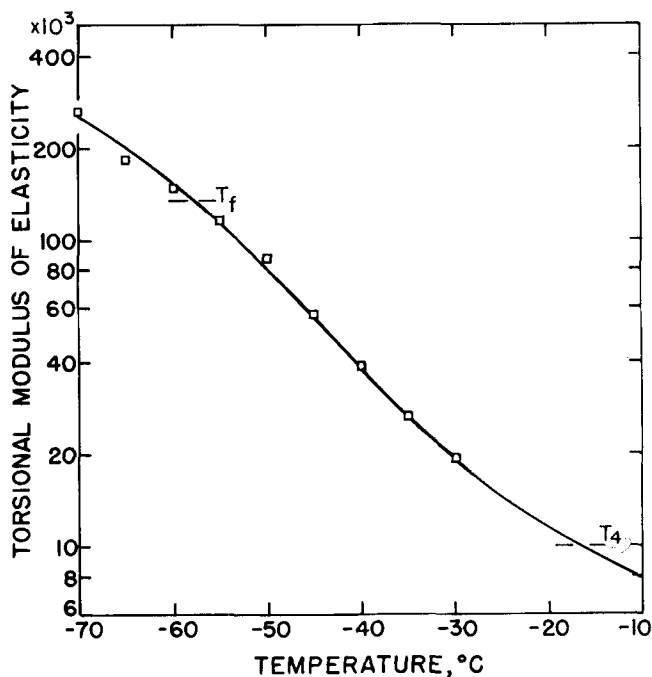

FIG. 1. Torsional stiffness curve for PVC compositions plasticized with N,N-dibutyloleamide; □, plasticized with dioctyl sebacate.
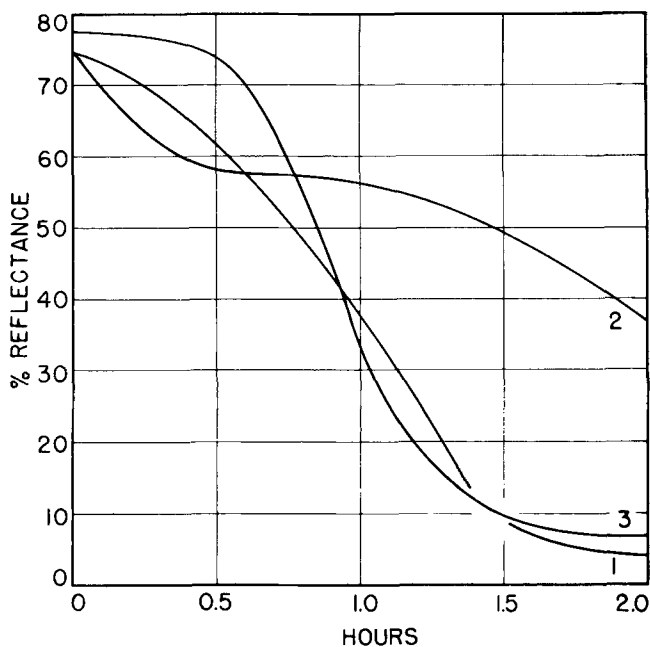
FIG. 2. Thermal stability of N,N-dibutylamide–PVC compositions (standard formulation).
Curve 1. N,N-dibutyloleamide.
Curve 2. N,N-dibutylepoxystearamide.
Curve 3. Di-2-ethylhexylphthalate (DOP).

FIG. 3. Thermal stability of N,N-dibutyloleamide—PVC compositions (various stabilizer formulations in parts per hundred parts of resin).
Curve 1. N,N-dibutyloleamide, standard formulation.
Curve 2. 55 N,N-dibutyloleamide, 3.2 T-360, 0.3 CH-300, 0.8 stearic acid.
Curve 3. 47 N,N-dibutyloleamide, 8 epoxysoybean oil, 3.2 T-360, 0.3 CH-300, 0.8 stearic acid.
Curve 4. 55 Di-2-ethylhexylphthalate, 3.2 T-360, 0.3 CH-300, 0.8 stearic acid.

too high a proportion of stearic or linoleic acid, are incompatible. This difficulty can be overcome for cottonseed oil, for example, by selective hydrogenation of the linoleic to the oleic acid moiety. The fatty acid mixture so obtained as well as animal acids and the unmodified fatty acid mixtures derived from *Limnanthes douglasii* seed and parsley seed oils (samples 22, 24, 26, 27) gave N,N-dibutyl amides which were good plasticizers. They were compatible and highly efficient and had brittle points approaching those of dioctyl adipate and dioctyl sebacate. Fatty acid mixtures having similar fatty acid compositional distributions might be employed advantageously in preference to the more expensive individual acids.

Figures 2 and 3 show the comparative thermal stabilities of N,N-dibutyloleamide-plasticized and DOP-plasticized polyvinyl chloride copolymer compositions after increasing periods of heating at 176C.

The compositions of Figure 2 were stabilized with basic lead carbonate. Curve 2 represents the thermal behavior of an N,N-dibutylepoxysteramide-plasticized composition. Neither of the amide compositions, Curves 1 and 2, exhibits as good a short-term stability as the DOP composition, Curve 3. On a long-term basis, however, the N,N-dibutyloleamide composition is comparable to the DOP composition and that of the N,N-dibutylepoxystearamide, Curve 2, is decidedly superior.

Compositions 2, 3, and 4 in Figure 3 were stabilized with a polymeric dibutyl tin mercaptide (Advastab T-360 from Carlisle Chemical Works, Inc.) in conjunction with an alkyl aryl phosphite chelator (Advastab CH-300). Curves 2 and 3 illustrate the tremendous improvement which can be achieved in the thermal stability of N,N-dibutyloleamide compositions upon replacing basic lead carbonate (Curve 1) by the tin mercaptide stabilizer-chelator system alone (Curve 2), or in conjunction with an epoxide stabilizer (Curve 3). Although these compositions fall short of the stability observed for a similarly
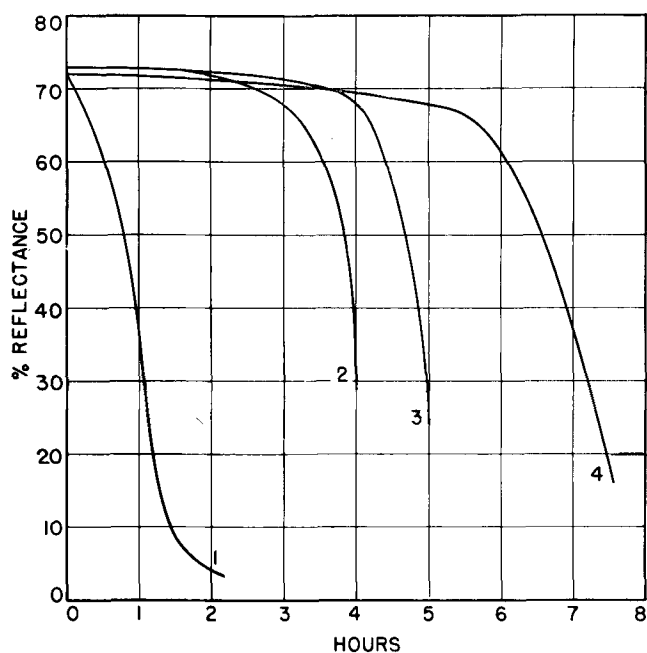
stabilized DOP composition (Curve 4) their stability is far superior to that of a DOP composition stabilized with basic lead carbonate (Figure 2, Curve 3). Although some modification in the tin stabilizer system will be necessary to overcome plating-out tendencies, the results nevertheless offer convincing evidence that thermal stabilization of amide plasticizers is not an insurmountable problem but rather one requiring a more systematic investigation.

The dialkyl amides as a class show excellent potential as PVC plasticizers because of their exceptional low-temperature properties and broad compatibilities. In one or both of these respects they are superior to many of the other amides already investigated, such as the morpholides, piperidides, and diesteramides. They should therefore be more attractive commercially, especially since they can be easily prepared from a wide range of commercial fatty acid mixtures and potentially cheap secondary amines.

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