tained since the disperse phase consists of the aggregated micelles (10) which are formed at the cloud point and above.

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# The Preparation and Plasticizing Characteristics of Piperidides of Long Chain Fatty Acids and N-Fatty Acyl Derivatives of Other Cyclic Imines[1]

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## Abstract

Forty-six N-acyl derivatives of cyclic imines have been prepared, characterized, and screened as primary plasticizers for poly(vinyl chloride-vinyl acetate) copolymer. Among these were the piperidides of decanoic, palmitic, stearic, oleic, erucic, ricinoleic, epoxystearic, epoxyoleic, diepoxystearic, sebacic, pinic, cottonseed, hydrogenated cottonseed, rapeseed, *Limnanthes douglasii*, animal, 2-ethylhexanoic, naphthenic, and dimer acids, as well as the N-oleoyl derivatives of a number of substituted piperidines and other cyclic imines including pyrrolidine, piperazine, hexamethylenimine, tetrahydroquinoline, 3-azabicyclo[3.2.2]nonane, dipyridylamine, and carbazole.

In general these amides of the 5-,6-, and 7-membered cyclic imines exhibited exceptionally high plasticizing efficiencies. The compatibilities observed were the best to date for fatty acid derivatives on the basis of both individual and ternary fatty acid composition-compatibility data. Several of these amides exhibited low-temp characteristics in the adipate plasticizer range without the adverse volatility characteristics of the adipates. There are indications that some of them have appreciable antifungal activity. It has been concluded that cyclic imines will, in general, produce fatty acid derivatives of better than average compatibility as vinyl plasticizers.

## Introduction

IN PREVIOUS PUBLICATIONS from this laboratory it was shown that the morpholides (1) and N-bis(acyloxyethyl)amides (2) of long chain fatty acids were in many instances acceptable plasticizers for vinyl chloride resins. This publication deals with the preparation, characterization, and plasticizer evaluation of a number of N-fatty acyl derivatives of various cyclic imines, including a study of the ternary composition-compatibility relations for the system N-oleoylpiperidine (OP), N-linoleoylpiperidine (LP), and N-palmitoylpiperidine (PP) with polyvinyl chloride resin. As a class, these amides also proved to be highly efficient primary plasticizers. Their compatibilities seem to be superior to any amides that we have so far examined.

[1] Presented at the AOCS Meeting in Minneapolis, 1963.
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## Experimental

The substituted piperidines were Reilly products; piperidine, 1,2,3,4-tetrahydroquinoline, 3-azabicyclo[3.2.2]nonane, pyrrolidine, and carbazole were Eastman Kodak chemicals; piperazine was obtained from Jefferson Chemical Co.; hexamethylenimine from Dupont Co. and N-methylpiperazine from Union Carbide Co. With the exception of oleic acid, which was Emery Industries Emersol 233 LL Elaine, and linoleic acid, which was a laboratory preparation of 95% purity, all acids were Eastman Kodak Co. products.

The densities were determined pycnometrically (3), the constant temp bath being controlled within 0.1C while the refractive indices were determined at 30.0 ± 0.1C with a precision Bausch and Lomb refractometer using the D sodium line.

With the exception of N-ricinoleoylpiperidine, N-oleoylcarbazole, the N-epoxyacylpiperidines, and N-oleoyl-4-(3-acetoxypropyl)piperidine, all of the compounds were prepared by the general procedure previously described by Magne et al. (4) or by the interaction of equimolar quantities of acid chloride and imine in the presence of pyridine. The N-ricinoleoylpiperidine was prepared from methyl esters as described by Dupuy et al. (5). The N-oleoylcarbazole was prepared by refluxing carbazole with a slight excess of oleoyl chloride in xylene for 4 hr, then removing the free acid by percolation through an alumina column. The N-epoxystearoylpiperidine was prepared by epoxidation of the N-oleoylpiperidine. The N-epoxyoleoylpiperidine and N-diepoxystearoylpiperidine were prepared by epoxidation of the N-linoleoylpiperidine.

N-Oleoyl-4-(3-acetoxypropyl)piperidine was prepared by slowly adding 50 g (0.17 mole) methyl oleate to a vigorously stirred mixture of 24.2 g (0.17 mole) 4-propanolpiperidine and 0.61 g (0.026 mole) metallic sodium dissolved in absolute methanol maintained at 65–70C under 60 mm pressure. The reaction was judged complete upon cessation of the evolution of methanol. The product of this reaction was found to be N-oleoyl-4(3-oleoxypropyl)piperidine (I). The desired product, N-oleoyl-4-propanolpiperidine (II) was obtained by a 24-hr cold saponification of the ester linkage in I, using 2.0 equivalents of alcoholic KOH, followed by acidification with HCl, solution in hexane, washing with water, and drying over anhydrous sodium sulfate. Any residual free

TABLE I
Analyses and Physical Properties of N-Acyl Derivatives of Various Cyclic Imines

| N-Acyl cyclic imines | Density 30°C | $n_D^{30}$ | MP °C | % C | | % H | | % N | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Exp. | Theory | Exp. | Theory | Exp. | Theory |
| N-2-Ethylhexanolypiperidine | 0.9190 | 1.4676 | | 77.43 | 73.81 | 11.82 | 11.83 | 6.52 | 6.63 |
| N-Palmitoylpiperidine | | | 37–38 | 78.02 | 77.88 | 12.70 | 12.77 | 4.32 | 4.33 |
| N-Stearoylpiperidine | | | 42–43 | 78.50 | 78.49 | 12.75 | 12.90 | 3.96 | 3.98 |
| N-Oleoylpiperidine | 0.8986 | 1.4773 | | 78.15 | 78.95 | 12.07 | 12.40 | 4.04 | 4.04 |
| N-Linoleoylpiperidine | 0.9255 | 1.4895 | | 79.00 | 79.40 | 11.77 | 11.89 | 3.92 | 4.03 |
| N-Erucoylpiperidine | 0.8972 | 1.4790 | | 79.84 | 79.86 | 12.61 | 12.67 | 3.48 | 3.41 |
| N-*Ricinoleoyl*piperidine | 0.9400 | 1.4870 | | 75.60 | 75.49 | 11.82 | 11.76 | 3.69 | 3.83 |
| N-Naphthenoylpiperidine | 0.9651 | 1.4945 | | | | | | 5.02 | 4.93 |
| Piperidide of animal acids | 0.9001 | 1.4745 | | | | | | 3.95 | 4.10 |
| Piperidide of hydrogenated cottonseed oil fatty acids | 0.8962 | 1.4761 | | | | | | 4.08 | 4.11 |
| Piperidide of *Limnanthes douglasii* oil fatty acids | 0.8976 | | | | | | | 3.63 | 3.70 |
| Piperidide of rapeseed oil fatty acids | 0.8961 | 1.4769 | | | | | | 3.56 | 3.77 |
| Piperidide of dimer acid (Empol 1014) | 0.9461 | 1.4983 | | | | | | 3.98 | 4.03 |
| N,N'-Sebacoyldipiperidine | | | 57–58 | 71.35 | 71.31 | 10.63 | 10.70 | 8.18 | 8.32 |
| N-Epoxystearoylpiperidine [a] | 0.9399 | 1.4769 | | | | | | | |
| N-Epoxyoleoylpiperidine [b] | 0.9538 | 1.4842 | | | | | | | |
| N-Diepoxystearoylpiperidine [c] | 0.9817 | 1.4796 | | | | | | | |
| N-Oleoyl-2-methylpiperidine | 0.8997 | 1.4764 | | 78.87 | 79.20 | 12.13 | 12.47 | 3.86 | 3.85 |
| N-Oleoyl-3-methylpiperidine | 0.8938 | 1.4757 | | 79.03 | 79.20 | 12.30 | 12.47 | 3.89 | 3.85 |
| N-Oleoyl-4-methylpiperidine | 0.8932 | 1.4758 | | 78.80 | 79.20 | 12.08 | 12.47 | 3.86 | 3.85 |
| N-Oleoyl-2-ethylpiperidine | 0.8997 | 1.4764 | | 79.21 | 79.44 | 12.51 | 12.55 | 3.64 | 3.71 |
| N-Oleoyl-4-ethylpiperidine | 0.8937 | 1.4763 | | 79.17 | 79.45 | 12.62 | 12.45 | 3.75 | 3.71 |
| N-Oleoyl-2-propylpiperidine | 0.9196 | 1.4756 | | 79.30 | 79.65 | 12.45 | 12.61 | 3.50 | 3.57 |
| N-Oleoyl-4-propylpiperidine | 0.8905 | 1.4757 | | 79.66 | 79.65 | 12.61 | 12.61 | 3.65 | 3.57 |
| N-Decanoyl-4-nonylpiperidine | 0.8847 | 1.4693 | | 78.69 | 78.78 | 12.90 | 12.96 | 3.76 | 3.83 |
| N-Oleoyl-4-nonylpiperidine | 0.8816 | 1.4748 | | 80.21 | 80.70 | 12.67 | 12.80 | 2.95 | 2.90 |
| N-Oleoyl-4-(5-nonyl)piperidine | 0.8865 | 1.4771 | | 80.62 | 80.70 | 12.80 | 12.80 | 2.99 | 2.90 |
| N-*Erucoyl*-4-*nonyl*piperidine | 0.8802 | 1.4759 | | 81.39 | 81.21 | 12.91 | 13.07 | 2.66 | 2.63 |
| N-Oleoyl-2-benzylpiperidine | 0.9386 | 1.5033 | | 81.73 | 81.74 | 11.17 | 11.44 | 3.12 | 3.18 |
| N-Oleoyl-4-benzylpiperidine | 0.8710 | 1.5061 | | 81.86 | 81.74 | 11.16 | 11.44 | 3.26 | 3.18 |
| N-Oleoyl-2,6-dimethylpiperidine | 0.8998 | 1.4765 | | 79.19 | 79.12 | 12.43 | 12.30 | 3.74 | 3.72 |
| N-Oleoyl-2-methyl-5-ethylpiperidine | 0.8980 | 1.4756 | | 79.51 | 79.66 | 12.40 | 12.51 | 3.79 | 3.85 |
| N,N'-Dioleoyldipiperidinomethane | 0.8973 | 1.4767 | | 78.52 | 79.30 | 12.14 | 12.19 | 3.94 | 3.94 |
| N-Oleoyl-4-(3-acetoxypropyl)piperidine | 0.9635 | 1.4777 | | 75.31 | 74.73 | 11.93 | 11.43 | 3.12 | 3.12 |
| Ethyl 2,2-dimethyl-3-(4-*n*-nonylpiperidino)carbonylcyclobutaneacetate | 0.9650 | 1.4774 | | 72.75 | 73.64 | 11.09 | 11.13 | 3.41 | 3.44 |
| Mixed piperidides of oleic acid [d] | 0.8915 | 1.4760 | | | | | | 3.63 | |
| N-Oleoylpyrrolidine | 0.9015 | 1.4766 | | 77.81 | 78.67 | 12.11 | 12.32 | 4.30 | 4.17 |
| N-Oleoylhexamethylenimine | 0.9127 | 1.4794 | | 78.83 | 79.21 | 12.11 | 12.46 | 3.79 | 3.85 |
| N-Oleoyl-1,2,3,4-tetrahydroquinoline | 0.9472 | 1.5093 | | 80.89 | 81.48 | 10.91 | 10.81 | 3.31 | 3.52 |
| N-Oleoyl-3-azabicyclo[3.2.2]nonane | 0.9364 | 1.4885 | | 79.20 | 80.09 | 11.95 | 12.06 | 3.40 | 3.60 |
| N-Oleoyl-2,2'-dipyridylamine | 0.9839 | 1.5238 | | 75.96 | 77.12 | 9.45 | 9.41 | 9.69 | 9.65 |
| N-Oleoylcarbazole | 1.0050 | 1.5569 | | 82.98 | 83.40 | 9.50 | 9.50 | 3.24 | 3.25 |
| N-Oleoyl-N'-methylpiperazine | 0.9156 | 1.4788 | | 74.47 | 72.44 | 11.63 | 11.62 | 7.43 | 7.68 |
| N,N'-Didecanoylpiperazine | | | 59–60 | 73.15 | 73.09 | 11.68 | 11.75 | 7.07 | 7.09 |
| N,N'-Dioleoylpiperazine | | | | 77.12 | 78.04 | 12.12 | 12.13 | 4.64 | 4.55 |

[a] *Oxirane content* 4.49%; *theory* 4.38%.
[b] Oxirane content 4.87%; theory 4.40%.
[c] Oxirane content 7.51%; theory 8.43%.
[d] Made from commercial byproduct mixture of alkylpiperidines.

acid was removed by percolating the dry hexane solution through a column of activated alumina, the amide being eluted with a 1:1 ethanol-benzene mixture. The amide recovered by stripping the eluate under reduced pressure gave no titration for either free acid or amine. Twenty-six g (0.06 mole) of (II) and 5.1 g pyridine (0.06 mole) were dissolved in 75 ml benzene and 5 g (0.06 mole) acetyl chloride added dropwise with stirring. After stirring for an additional hr the reaction mixture was filtered, washed successively with dilute HCl and water, dried over anhydrous sodium sulfate, and the solvent removed by stripping under reduced pressure.

*Plasticizer Screening.* These amides were all screened as plasticizers for 95% polyvinyl chloride—5% polyvinyl acetate copolymer (Vinylite VYDR) and a few of these were given an additional screening with the homopolymer (Geon 101). The compound formulation used was:

| | |
|---|---|
| Vinylite VYDR or Geon 101 | 63.5% |
| Plasticizer | 35% |
| Stearic acid | 0.5% |
| Basic lead carbonate | 1.0% |

The milling, molding, and testing procedures followed those previously reported (1,6) except for the use of 10–15 mil sheets in the volatility and stability tests. Compositions which showed no exudation or smearing tendencies during 90 days shelf storage or 60 days' exposure to north window light were rated compatible. Thermal stabilities were rated as better, poorer, or equal to that observed for the di-2-ethylhexylphthalate (DOP) control composition.

The evaluation of some of these materials as Buna N (Hycar 1042-33% acrylonitrile) softeners was conducted by standard procedures (7).

Soil burial tests (8) were conducted for some of these plasticized stocks to determine antimicrobial activity. Five 10–15 mil specimens of each composition were placed in a soil bed and examined weekly for evidence of discoloration.

## Results and Discussion

Table I shows the densities, refractive indices, melting points, and elemental analyses of the various fatty amides. The results for the plasticizer evaluation in Vinylite VYDR and Geon 101 resins are given in Table II.

The data for Samples 1–17 show that the amides of the unsubstituted piperidines, wherein the acid moiety is that of an unsubstituted $C_{16}$ saturated or a $C_{18}$ to $C_{22}$ monounsaturated monobasic aliphatic acid, have better modulus, elongation, brittle point, and volatility-loss characteristics than the control, DOP.

Shortening, branching or substitution of the acyl chain, on the other hand, adversely influences low temp performance and, in some instances, volatility. The performance of Samples 1,6,7,15,16, and 17 is illustrative of this effect. This is not surprising in the light of similar findings observed in ester type plasticizers (9) and the morpholides (5,10).

The piperidides of all the naturally occurring acid mixtures tested, except those of cottonseed oil, exhibit exceptionally good compatibility characteristics, in most instances comparable to N-oleoylpiperidine. This is most apparent in the animal and rapeseed acid mixtures where the stearic or linoleic acid level has been found to be a factor adversely affecting the

TABLE II

Physical Characteristics of Vinyl Chloride-Vinyl Acetate Copolymer Stocks Plasticized with N-Fatty Acyl Derivatives of Cyclic Imines (35% Plasticizer)

| Sample Number | Plasticizer | Tensile strength | 100% modulus | Elongation | Brittle point | Volatility loss | Compatibility [a] | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | Shelf storage | North window |
| | | psi | psi | % | °C | % | | |
| 1 | N-2-Ethylhexanoylpiperidine | 2110 | 1040 | 290 | −27 | 11.74 | C | C |
| 2 | N-Palmitoylpiperidine | 2680 | 1160 | 350 | −35 | 1.08 | C | C |
| 2 | N-Palmitoylpiperidine [b] | 2840 | 1300 | 350 | −37 | ..... | C | I |
| 3 | N-Stearoylpiperidine | 2770 | 1290 | 360 | −29 | ..... | I | I |
| 4 | N-Oleoylpiperidine | 2670 | 1170 | 390 | −47 | 1.18 | C | C |
| 4 | N-Oleoylpiperidine [b] | 2990 | 1400 | 330 | −41 | ..... | C | C |
| 5 | N-Erucoylpiperidine | 2890 | 1380 | 400 | −49 | 0.49 | C | C |
| 6 | N-Ricinoleoylpiperidine | 3180 | 1700 | 380 | −29 | 5.40 | C | C |
| 7 | N-Naphthenoylpiperidine | 3110 | 1690 | 340 | +1 | 11.92 | C | C |
| 8 | Piperidide of animal acids | 2710 | 1180 | 370 | −39 | 0.88 | C | C |
| 9 | Piperidide of cottonseed oil fatty acids | 2560 | 1200 | 330 | −45 | ..... | I | I |
| 10 | Piperidine of hydrogenated cottonseed oil fatty acids | 2660 | 1220 | 370 | −45 | 0.38 | C | C |
| 11 | Piperidide of *Limnanthes douglasii* oil fatty acids | 2770 | 1360 | 370 | −45 | 1.36 | C | C |
| 12 | Piperidide of rapeseed oil fatty acids | 2750 | 1300 | 340 | −53 | 0.57 | C | C |
| 13 | Piperidide of dimer acid (Empol 1014) | 3190 | 2630 | 180 | −3 | 0.07 | C | C |
| 14 | N,N'-Sebacoyldipiperidine | 3040 | 1650 | 330 | +7 | 0.30 | C | C |
| 15 | N-Epoxystearoylpiperidine | 2810 | 1180 | 340 | −21 | 0.54 | C | C |
| 16 | N-Epoxyoleoylpiperidine | 2550 | 1170 | 330 | −23 | 0.63 | C | C |
| 17 | N-Diepoxystearoylpiperidine | 2730 | 1200 | 340 | −11 | 0.61 | C | C |
| 18 | N-Oleoyl-2-methylpiperidine | 2470 | 1240 | 310 | −39 | 0.83 | C | C |
| 19 | N-Oleoyl-3-methylpiperidine | 2500 | 1170 | 330 | −43 | 0.79 | C | C |
| 20 | N-Oleoyl-4-methylpiperidine | 2520 | 1240 | 310 | −43 | 0.65 | C | C |
| 21 | N-Oleoyl-2-ethylpiperidine | 2880 | 1390 | 360 | −45 | 1.20 | C | C |
| 22 | N-Oleoyl-4-ethylpiperidine | 2760 | 1280 | 390 | −45 | 0.47 | C | C |
| 23 | N-Oleoyl-2-propylpiperidine | 3050 | 1680 | 320 | −33 | 0.34 | C | C |
| 24 | N-Oleoyl-4-propylpiperidine | 2950 | 1410 | 370 | −45 | 1.01 | C | C |
| 25 | N-Decanoyl-4-nonylpiperidine | 2880 | 1350 | 390 | −39 | 0.55 | C | C |
| 26 | N-Oleoyl-4-nonylpiperidine | 2780 | 1700 | 330 | −51 | 0.27 | C | C |
| 27 | N-Oleoyl-4-(5-nonyl)piperidine | 2990 | 1750 | 340 | −39 | 0.38 | C | C |
| 28 | N-Erucoyl-4-nonylpiperidine | 1930 | 1720 | 160 | −27 | 1.97 | C | C |
| 29 | N-Oleoyl-2-benzylpiperidine | 3260 | 1740 | 320 | −23 | 0.56 | C | I |
| 30 | N-Oleoyl-4-benzylpiperidine | 3160 | 1730 | 320 | −23 | 0.21 | C | C |
| 31 | N-Oleoyl-2,6-dimethylpiperidine | 2990 | 1430 | 360 | −37 | ..... | C | C |
| 32 | N-Oleoyl-2-methyl-5-ethylpiperidine | 2870 | 1340 | 380 | −37 | 0.40 | C | C |
| 33 | N,N'-Dioleoyldipiperidinomethane | 2840 | 1190 | 390 | −49 | 1.30 | C | C |
| 34 | N-Oleoyl-4-(3-acetoxypropyl)piperidine | 2950 | 1260 | 380 | −29 | 0.58 | C | C |
| 35 | Ethyl 2,2-dimethyl-3-(4-*n*-nonylpiperidino)carbonylcyclobutaneacetate | 3180 | 1860 | 320 | −1 | 2.53 | C | C |
| 36 | Mixed piperidides of oleic acid [c] | 2730 | 1290 | 350 | −43 | ..... | C | C |
| 37 | Mixed piperidides of oleic acid [d] | 2910 | 1380 | 370 | −43 | 0.67 | C | C |
| 38 | N-Oleoylpyrrolidine | 2400 | 990 | 370 | −47 | 0.00 | C | B |
| 39 | N-Oleoylhexamethylenimine | 2650 | 1300 | 350 | −49 | ..... | C | .... |
| 40 | N-Oleoyl-1,2,3,4-tetrahydroquinoline | 2990 | 1470 | 350 | −39 | 1.55 | C | I |
| 41 | N-Oleoyl-3-azabicyclo[3.2.2]nonane | 3000 | 1580 | 310 | −35 | 1.08 | C | B |
| 42 | N-Oleoyl-2,2'-dipyridylamine | 3500 | 1870 | 340 | −27 | 9.53 | C | I |
| 43 | N-Oleoylcarbazole | 3500 | 2500 | 300 | −23 | ..... | I | I |
| 44 | N-Oleoyl-N'-methylpiperazine | 2510 | 1810 | 280 | −43 | ..... | I | I |
| 45 | N,N'-Didecanoylpiperazine | 2830 | 1770 | 250 | −23 | ..... | I | I |
| 46 | N,N'-Dioleoylpiperazine | 2880 | 1330 | 380 | −37 | ..... | I | I |
| | Di-2-ethylhexylphthalate (control) | 3050 | 1610 | 330 | −33 | 1.50 | C | C |
| | Dioctyl adipate (control) | 2890 | 1290 | 380 | −55 | 6.00 | C | C |

[a] C = Compatible, B = borderline, I = incompatible.
[b] Polyvinyl chloride (Geon 101).
[c] Mixture of 45%,40% and 15% by wt of samples 19,20, and 31, respectively.
[d] Made from commercial byproduct mixture of alkylpiperidines.

compatibility of other substituted amides (10). In addition, these piperidides exhibit excellent low-temp and volatility characteristics.

Samples 36 and 37, the mixed alkylpiperidides of oleic acid, the former a synthetic mixture of Samples 19,20, and 31, respectively, and the latter prepared from a cheap commercial byproduct of mixed alkylpiperidines, show, on the whole, better plasticizing characteristics than the control, DOP. This is not surprising in view of the performances of the individual N-oleoylalkylpiperidines.

The data for the amides of the substituted piperidines, Samples 18–37, show that within the limits of the experimental observations, alkylation decreases volatility loss without apparently adversely affecting compatibility. Though the data are scant, the north window compatibility test indicates that monosubstitution in the 2-position of the piperidine ring is detrimental to compatibility, whereas monosubstitution in the 4-position or disubstitution enhances or has no adverse effect on compatibility.

A comparison of N-oleoyl-4-(3-acetoxypropyl)piperidine (Sample 34) with N-oleoyl-4-propylpiperidine (Sample 24) shows that the substitution of an acyloxyalkyl for an alkyl substituent in the piperidine ring while conferring improved efficiency and volatility to the product also causes a considerable loss in low-temp performance. Conversely, comparison of the data for ethyl 2,2-dimethyl-3-(4-nonylpiperidino) carbonylcyclobutaneacetate (Sample 35), an ester amide not involving ring substitution, with those of N-2-ethylhexanoylpiperidine (Sample 1) shows that while the introduction of the ester group results in improved tensile strength, elongation, and volatility, it also has an adverse effect on low-temp properties. On the basis of these limited observations it is obvious that while the effects of a supplemental ester group on the overall plasticizing properties of these amides cannot be clearly defined, the one apparently consistent influence has been its adverse effect on low-temp characteristics. However, even this may itself be reversed when longer acyl or alkoxy groups are involved. Results obtained for Samples 38–46 in general show that the compatibility is adversely affected when the imine is predominantly aromatic.

There appears to be a general tendency toward retrograde plasticizing properties amongst diamides (Samples 13,14,44,45, and 46) whether derived from diamines or dibasic acids. This is in striking contrast to the esters of dibasic acids which, in general, exhibit desirable plasticizing properties. It must be concluded that amidification is not a modification conducive to desirable plasticizing properties in moderate length dibasic acids.

The only noncyclic imine (Sample 42) which was evaluated proved to be compatible by shelf storage

TABLE III
Properties of Buna-N Stock Plasticized with Various N-Acylpiperidines

| Plasticizer | Tensile strength | | Elongation | | 300% Modulus | | Shore A hardness 10 sec | Wt loss | Brittle point | Vol change after 72 hr at 78F | Compatibility [b] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Unaged | Aged [a] | Unaged | Aged [a] | Unaged | Aged [a] | | | | | |
| | psi | psi | % | % | psi | psi | | % | °C | % | |
| N-Oleoylpiperidine | 1940 | 2140 | 710 | 510 | 600 | 990 | 50 | 0.52 | −48 | 22.2 | I |
| Piperidide of hydrogenated cottonseed oil fatty acids | 1850 | 1950 | 700 | 510 | 560 | 1000 | 52 | 0.96 | −48 | 22.5 | I |
| Mixed piperidides of oleic acid | 1910 | 1930 | 680 | 500 | 590 | 1050 | 53 | 0.94 | −48 | 22.9 | I |
| Dibutylsebacate (control) | 2170 | 2350 | 580 | 370 | 960 | 1920 | 55 | 5.52 | −55 | 20.9 | C |

[a] Aged for 48 hr in air oven at 212F.
[b] C = Compatible, I = incompatible, failed in about 4 months.

test but failed in the north window test in less than 15 days.

N-Palmitoylpiperidine and N-oleoylpiperidine were evaluated in polyvinyl chloride homopolymer (Geon 101). These compositions showed, as expected, better tensile strength but poorer modulus and compatibility in the north window test than similar copolymer (VYDR) compositions. Although the Geon 101 composition for N-oleoylpiperidine passed the north window test, it failed after 128 days. On the basis of these limited observations it would appear that this family of plasticizers will perform, as might be expected, somewhat less efficiently in this resin than in the copolymer.

Thermal stability determined for a number of these nonepoxidized plasticizers indicates that all are inferior to DOP. The epoxidized samples showed better thermal stability than DOP, but at a sacrifice of low-temp performance.

Soil burial tests for N-oleoylpiperidines show that antimicrobial activity increased in the order piperidide, 2-methylpiperidide, mixed alkyl piperidides, 2,6-dimethylpiperidide, and DOP. All the piperidide-plasticized compositions became yellow and stiff and, with the exception of the N-oleoyl-2,6-dimethylpiperidine, developed pink spots.

Soapy water extractability determinations indicated that the plasticized stocks are comparable to the morpholides but inferior to DOP.

The ternary composition-compatibility diagram, Figure 1, was constructed for the system OP-LP-PP following the general procedure previously reported for the corresponding morpholides (9). Although

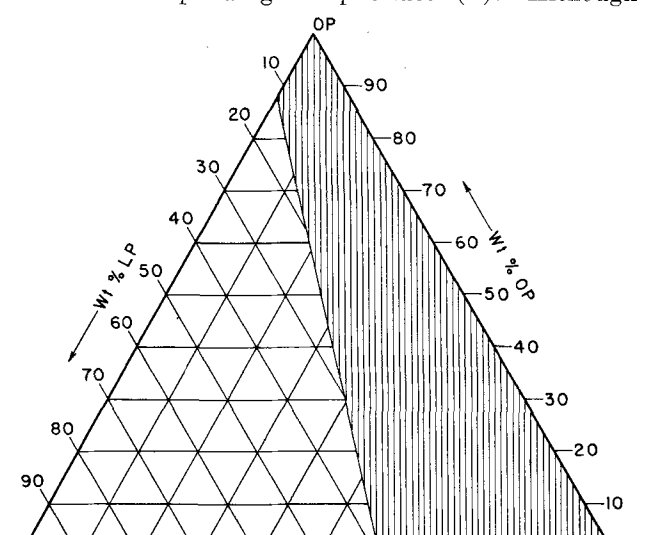


FIG. 1. Ternary composition-compatibility diagram for the system OP-LP-PP. Shaded area represents all compatible compositions.

the boundary of the compatible region (shaded area) is only approximate, within ca. 5%, the superior compatibility of the piperidides is well demonstrated by the broader compositional area of the compatible region as compared to the much more restricted area for the same fatty acid morpholides (9). This ternary diagram can be used to predict the compatibility performance of any piperidide mixture of these fatty acids as well as the adjustments in composition necessary to bring fatty acid mixtures within the compatible region.

*Nitrile Rubber Softeners.* N-Oleoylpiperidine, piperidide of hydrogenated cottonseed oil fatty acids, and mixed N-oleoylalkylpiperidines (Samples 4,10, and 37) were evaluated as softeners for nitrile rubber (Hycar 1042-33% acrylonitrile). The following formulation was employed in the evaluations:

| | |
|---|---|
| Nitrile rubber | 100.0 parts |
| SRF black | 60.0 parts |
| Zinc oxide | 5.0 parts |
| Stearic acid | 1.5 parts |
| Sulfur | 1.5 parts |
| Benzothiazyldisulfide | 1.5 parts |
| Softener | 20.0 parts |

The milling, curing, and testing procedures were the same as those of Fore, et al. (7).

The results, reported in Table III, indicate that piperidides are more efficient but less compatible softeners for nitrile rubber than the control (dibutylsebacate), yielding softer stock, as indicated by Shore A hardness, and they appear to exhibit better accelerated aging characteristics. The superior aging properties could result in part from the vastly superior volatility characteristics of the piperidides under the test conditions. In low-temp performance, compatibility, and resistance to the swelling action of solvents, i.e. volume change, the piperidides are not quite as good as the control.

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