Wax Compositions from N-Allylstearamide and N-Allyl Hydrogenated Tallow Amides, by Reaction with Benzoyl Peroxide

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Abstract

When either pure N-allylstearamide or mixed allylamides, made by the aminolysis of hydrogenated tallow, were heated at 90C for 3 hr with benzoyl peroxide, the reaction products were medium-hard, high-melting (ca. 70–80C) waxes of light color suitable for use in polish applications. Hardness increased with increase in benzoyl peroxide, reaching an optimum for 3 to 8 g of peroxide per 100 g amide. Qualitative floorwear tests on films obtained from paste and emulsion compositions showed the allylamide waxes to be inferior to carnauba and a Fisher-Tropsch wax, but superior to several other synthetic waxes including polyethylene. No special property advantage was found using pure allylstearamide. Resistance to oxidation at 90C was good and the waxes emulsified readily.

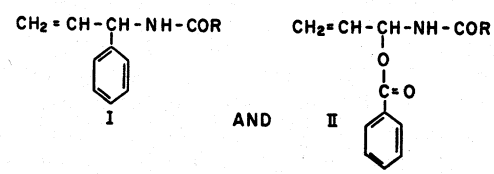
In the reaction of allylstearamide with benzoyl peroxide, polymer formation depends strongly on catalyst concentration ($dM/dP = 2$, compared to 14–50 for allyl esters) and some products of substitution and induced decomposition are formed. Wax properties were related to polyallylstearamide content.

Introduction

HARD AND MEDIUM-HARD waxes of both natural and synthetic origin have long been used in polishing and surface-coating applications (1,2). Surface coatings employing polymeric substances, usually in mixtures with natural and synthetic waxes, have become especially important in the polish industry in the last decade. Vinyl polymers used have included polyethylene (1–3), polyvinyl chloride (3), polyvinyl acetate (3) and stearate (2), acrylics (3), polystyrene (3,4), silicone polymers (5), polyvinylidene fluoride (6), and polypropylene (7). Allylic polymers and copolymers used have been cyclohexyl allyl maleate (8) and allyl stearate-maleic anhydride (9). With the exception of the polyenes and polyvinyl stearate, these substances are not themselves waxes, but act to extend a true wax, and confer good mechanical properties and light color on films containing waxes, especially when used in dry-bright formulations. Such polymers are blended with compounds carrying long chains, as frequently encountered in natural or synthetic waxes.

In the course of an investigation of homopolymerization of the allylic monomer N-allylstearamide (10), it was observed that hard and medium-hard waxes resulted from the treatment of the monomer at 90C for 3 hr with quantities of benzoyl peroxide insufficient to transform most of the amide to products. Similar results were obtained for allylamides prepared from hydrogenated tallow. Because waxes consisting of high-melting amides and containing polymer might have value in polishing applications, the physical properties of compositions prepared over a range of added benzoyl peroxide were evaluated, using both pure N-allylstearamide and mixed tallow amides, the latter easily prepared by the aminolysis of hydrogenated tallow (11). The purpose of this report is to describe these properties and compare the results with those found for representative commercial waxes.

The polymerization behavior of N-allylstearamide and other allylamides (10) is markedly different from that of allyl esters and certain other allylic compounds (12) in that relatively little polymer is formed when they are treated with a catalytic amount of peroxide. The ratio of monomer consumed to peroxide destroyed (dM/dP) for N-allylamides is a constant equal to about 2 compared with 14 to 15 (13,14) for allylacetate. This results from an unfavorable competition for the benzoyloxy radicals, produced by thermal decomposition of the initiator owing to transfer at the allylic methylene group. Phenyl and benzoate derivatives of the monomer having structures I and II, respectively, are formed together with benzoic acid and benzene.



Although polymer formation is thus retarded, peroxide consumption is rapid because of induced effects (10), and the polymer that is formed has the low degree of polymerization ($\overline{DP}$) of about 10 characteristic of allylic homopolymers. The homopolymer as an isolated product is a soft wax with poor mechanical properties. However, when moderate amounts of peroxide are used and monomer and polymer are not separated, waxes are produced because of changes in the overall morphology of the system.

Experimental

Preparation of the Allylamides

N-Allylstearamide was prepared from 99% pure methyl stearate. Mixed tallow amides were prepared from fully hydrogenated tallow (Wilson-Martin Wilvar 1000) used without purification; composition specifications were: myristic 3%, palmitic 29%, stearic 67%, oleic 1%. Commercial beef tallows typically vary ± 2 to 5% in major components and ± 10% to 20% in minor components. Such variation should not appreciably affect the physical measurements reported. Both pure and mixed amides were prepared in batches using 174 g of the appropriate ester. The reactions were run in crown-capped bottles at 70C for 24 hr, using the procedure and proportions of experiment 2 of reference 11. The crude reaction product was isolated as in the reference procedure and crystallized

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TABLE I

Wax emulsified	Parts/100			
	Wax	Oleic acid	Morpholine	Water
Carnauba, N.C. 3	12.8	2.24	1.92	83.1
A-C Polyethylene, 629	16.7	3.33	3.33	76.7
Duroxon J-324	15.0	1.00	1.70	82.0
Mixed tallow amides, 4M %	12.8	2.20	1.90	83.1
Mixed tallow amides, 6M %	12.8	2.20	1.90	83.1

twice from acetone (10 ml/g) at 0C. Results were: Pure N-allylstearamide: yield 85.3%; mp 83.8–84.3C; ester No. 0.0; % carbon, calcd. 77.93, found 77.61; % hydrogen, calcd. 12.77, found 12.70; % nitrogen, calcd. 4.33, found 4.31. Mixed tallow amides: yield 75.6%; mp 75.0–79.0C; ester No. 0.0; % carbon, calcd. 77.71, found 77.99; % hydrogen, calcd. 12.72, found 12.91, % nitrogen, calcd. 4.46, found 4.43.

Preparation of Waxes

Chosen quantities of benzoyl peroxide were added in small increments (0.1 to 0.2 g) to 50 g of amide in flasks maintained at 90C as described (10), except that the flasks were open to permit escape of benzene and carbon dioxide. Heating was continued for 3 hr after the addition of the last increment of the peroxide, to complete consumption of the initiator. Unless extracted, the crude reaction mixture was poured into appropriate molds for testing.

Removal of Benzoic Acid

Selected mixed amide waxes (Expts. 10, 11, 12, 13 of Table IV) were dissolved in benzene, 5 ml/g, washed 4 times with equal volumes of 10% sodium carbonate solution at 60C, freed of alkali, dried over calcium sulfate, and isolated by evaporation. Acid values after extraction ranged from 0.34 to 0.84, while saponification values remained unchanged. In another procedure, the wax (Expt. 12), in the form of an oil was treated at 90C three times with 10% aqueous sodium carbonate (7.5 ml/g), freed of alkali, washed once with 10% HCl, freed of acid and dried. The acid treatment caused some darkening of the oil. Acid value was 1.59 and the saponification value was unchanged. In a third method, a wax, prepared using 4 mole % peroxide, was subjected at both 90C and 150C to a pressure of 2 mm Hg, and acid removal was followed as a function of time by acid value. Although little reduction in acid occurred at 90C in 10 hr, at 150C the acid value was gradually reduced to 1.2 in 4 hr, and further reduction in 10 hr was very small. Negligible differences in physical properties were observed between the extracted and unextracted waxes, but the extracted samples showed greatly reduced exudation of benzoic acid. Benzoic acid was insoluble and thus caused some haze to develop in films from unextracted waxes.

Evaluation as Floor Waxes

The paste compositions which were prepared are given, parts per hundred: Commercial waxes: wax 31.2, mineral spirits 59.9, turpentine 8.9. Allylstearamide waxes: wax 37.6, mineral spirits 54.3, turpentine 8.13. The allylamide waxes were prepared using the following quantities of benzoyl peroxide, g/100 g amide: 1.55, 2.32, 3.09, 4.64, 6.18. All waxes were prepared by evaporation of benzene solutions after extraction to remove benzoic acid. Although for optimum performance it is customary to use blends of waxes, in the present pastes, in order to permit meaningful comparisons, single waxes were used. Because the solubilities of the allylstearamide waxes, especially those made from mixed tallow amides, were higher than those of the commercial waxes, their pastes were somewhat more fluid. No attempt was made to optimize any recipe. A single coat of wax was applied to a clean section of the floor in a well-travelled area and buffed. Films were checked once a week for gloss, wear, and repolishing characteristics.

Emulsions were also make using the recipe shown in Table I. The wax, melted with the oleic acid and morpholine, was blended into the water at 98C with rapid mechanical stirring.

TABLE II

Calculated Composition of Waxes Prepared from Mixed Tallow Amides[a]

Benzoyl peroxide g/100 g[b]	Wax composition, g/100 g amide				
	Benzoic acid	Benzoate-substituted amide	Phenyl-substituted amide	Polymer	Amide unreacted[c]
0.39	0.22	0.44	0.11	1.29	98.3
1.55	0.89	1.76	0.43	5.06	93.4
2.32	1.33	2.64	0.65	7.51	90.0
4.64	2.67	5.28	1.29	14.5	80.7
7.73	4.44	8.80	2.16	22.9	69.0
9.27	5.33	10.6	2.6	26.8	63.4

[a] Composition of the waxes from pure N-allylstearamide were very similar.
[b] Corresponds to experiments 9 through 14 of Table IV.
[c] Uncorrected for the substituted amide entering the polymer. In the last experiment listed above, the unreacted amide so corrected is 66.03, assuming monomer reactivity ratios $r_1 = r_2 = 1$.

Results and Discussion

Composition and Physical Properties

In Table II are listed the approximate compositions of the waxes prepared from mixed tallow amides. The compositions of the waxes made from pure N-allylstearamide were very similar. These compositions were calculated using constants which relate byproduct formation linearly, and polymer formation exponentially, to the amount of peroxide employed (10). The characteristic constants for N-allylstearamide are listed in Table III. In some instances, the compositions calculated were verified experimentally in this investigation.

The physical properties of the waxes prepared from both pure N-allylstearamide and mixed tallow amides are listed in Table IV together with the physical properties of selected commercial waxes determined by the same testing methods. Melting points decreased with increase in initiator content and those for the pure-amide waxes were somewhat higher than for the mixed-amide waxes, as would be expected. All melting points were in a useful range, however.

Hardness was determined by two methods in common use, namely, Shore and needle penetration (1), and by a third method (15) based on the Brinell hardness test for metals. In the last procedure, elastic modulus is a function of the depth of penetration of a steel ball under constant load for short periods. In

TABLE III

Constants for Calculation of Product Concentrations in the Reaction of N-Allylstearamide with Benzoyl Peroxide at 90C[a]

Product concentration, eq/kg amide	Constant, m
Benzoic acid	0.570
Benzene	0.086
Amide, substituted by benzoate	0.320
Amide, substituted by phenyl	0.087
Amide, entering polymer[b]	−0.1771[b]

[a] The relationship is: $[P] = m[I] + b$, where $[P]$ = byproduct concentration, eq/kg amide; $[I]$ = initiator concentration, eq/kg amide; and $b = o$.
[b] The relationship is: $a\text{-}x = a_o \exp(-0.1771\ P_o/2.303)$ where $a\text{-}x$ is the mole fraction amide remaining, P_o is initiator concentration, eq/kg, and $a_o = 1$. $1\text{-}(a\text{-}x)$ equals the mole fraction of amide entering polymer.

TABLE IV

Physical Properties of Waxes Prepared from N-Allylstearamide (and of Selected Commercial Waxes)

Experiment No.	Benzoyl peroxide, g/100 g amide	mp Capillary, C	Hardness[c] Shore[d]	Needle penetration[e] (mm × 10)	Brinell kg cm^{-2}[f]	Tensile lb. in^{-2}[g]	Color Gardner (melt)	Density
Pure allyl stearamide[a]								
1	0	84.0–84.5	76.4	14.7	51.6	14.2	..	
2	0.37	83.5–84.5	99.7	1.1	290.6	377	3	
3	1.50	82.0–83.5	99.1	1.5	152.1	246	6	
4	2.25	81.0–82.0	98.5	1.6	176.9	267	6	
5	4.50	79.5–80.5	98.6	2.2	204.0	169	7	
6	7.50	77.5–78.8	98.5	3.0	176.8	...	8	
7	8.98	75.5–77.5	98.5	3.6	160.0	197	..	
Allyl mixed tallow amides[a]								
8	0	75.0–79.0	64.3	15.1	57.1	.....	..	.....
9	0.39	75.0–78.0	94.1	7.1	91.7	.....	3	0.9363
10	1.55	72.0–77.0	96.5	4.8	124.9	.....	5	0.9237
11	2.32	70.0–76.0	98.0	4.7	127.7	.....	6	0.9054
12	4.64	69.0–75.0	98.9	4.2	173.3	.....	9	0.9451
13	7.73	63.0–70.0	97.7	6.1	161.2	.....	..	0.9611
14	9.27	60.0–67.5	95.2	7.2	143.5	.....	..	0.9648
Commercial waxes:								
15	Carnauba Yellow 1	82.0–84.0	99.9	0.7	338.5	518	9	
16	Carnauba N.C. 3	82.0–83.5	100.0	1.1	426.6	249	17	
17	Mod. Fischer-Tropsch[h]	83.5–92.0	99.6	1.6	262.5	.....	10	
18	Methylene-bis-stear-amide[i]	128.0–133.0	99.3	1.7	291.7	.....	7	
19	Hydrogenated Tallow	59.0–61.0	96.4	5.9	148.2	.....	1	
20	Polyethylene[j]	90–98.0	94.5	5.9	132.5	.....	1	
21	Microcryst. 190/200F	88–94	93.2	4.8	107.9	244	1	
22	Paraffin 135/137F	57–58	75.4	12.3	88.6	137	1	
23	Beeswax	62–64[b]	.....	18.0	21.7	....	10	
24	Polyvinylstearate	45–48[b]	99.2	1.0	...	301	....	
25	Candelilla	76–77[b]	98.1	2.2	164.6	270	15	

[a] Corresponds to the following mole %, respectively: 0, 0.5, 2.0, 3.0, 6.0, 10.0, 12.0. Data were also obtained using 0.25, 1.0, 4.0, 8.0 mole % peroxide and are included in Fig. 1.
[b] From literature references (1,2).
[c] Run on unextracted samples.
[d] Shore Durometer hardness, ASTM D 676–58T.
[e] ASTM 1321–57T, 5 sec., 100 g, top wt.
[f] Reference (15). Average deviation, ± %, 0.75; extremes 0.19 and 2.2. Run at 23C, rel. humidity 50%.
[g] ASTM D 1320–60T, but using Instron Tensile Tester Model TT-B with constant cross-head of loading. Average deviation, %, 15.01, extremes 7.5 and 25.1. Samples not extracted.
[h] Duroxon J 324.
[i] Armowax.
[j] A-C Polyethylene 629.

the method as modified for use with fats and waxes, a hardness index number is obtained, in units of kilograms per square centimeter, that expresses the ratio of the weight of the ball to the ratio of ball to indentation diameters. As noted by Lovegren, Guice and Feuge (15) and as can be seen from the present data, this method shows considerably more sensitivity for hard materials than do the penetration and Shore methods. Hardness increased for the mixed allylamides, rising from low values at low peroxide content and passing through a maximum when about 4.6 g of peroxide/100 g of amide (Expt. 12) was used. With the pure amide, hardness increased very rapidly at very low catalyst concentrations, passed through a sharp maximum at 0.37 g peroxide/100 g amide (Expt. 2), and then reached a second maximum in the same range and at a hardness index (Expt. 5) similar to that of the mixed tallow amides. This is illustrated graphically in Figure 1.

Relative crystal size was determined by measuring the characteristic crystal pattern widths under a microscope and expressing the data relatively in arbitrary units. When relative crystal size was plotted as a function of initiator concentration in the same figure, low values were found in the region of maximum hardness. With the pure amide, the smallest crystal sizes coincided with the second maximum; in the region of the first sharp maximum, crystal size was quite large. This suggests that the pure amide specimen possessed a gradient of crystal packing having special hardness at the surface, which was the region of measurement. In the region of maximum hardness these waxes consisted of plates closely resembling crude montan wax (16).

In general, the compositions may be classified as medium-hard waxes. The hardest compositions, while considerably softer than carnauba wax, a modified Fischer-Tropsch wax, and methylene-bis-stearamide (Armowax), are considerably harder than a polyethylene wax, hydrogenated tallow, microcrystalline wax and paraffin. Tensile properties (Table IV) were characteristic of brittle materials and were similar for all of the waxes.

Needle penetration hardness as a function of temperature for experiments using 1 and 8 mole % benzoyl peroxide are compared (Fig. 2) with values found for both carnauba (Expt. 16) and microcrystalline wax (Expt. 21). The wax made with 1 mole % peroxide resisted deformation over a range of temperatures about as well as carnauba, and the 8 mole % material was intermediate with respect to the two commercial waxes.

Color (Table IV) increased with increase in peroxide used; in the optimum hardness regions (Expt. 4–6; 11–13) Gardner color was similar to that of

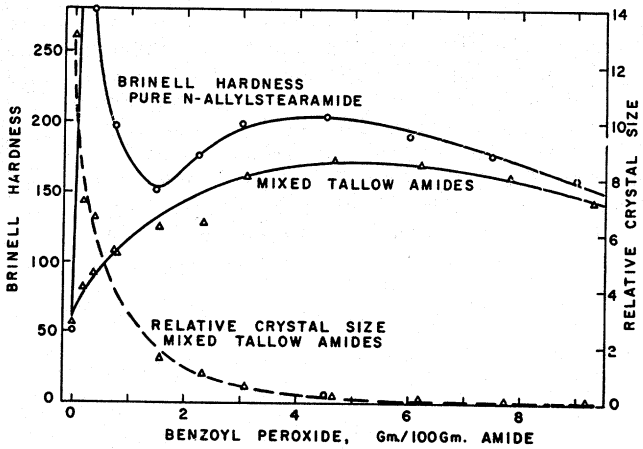

FIG. 1. Comparison of Brinell hardness and relative crystal size with initiator concentration.

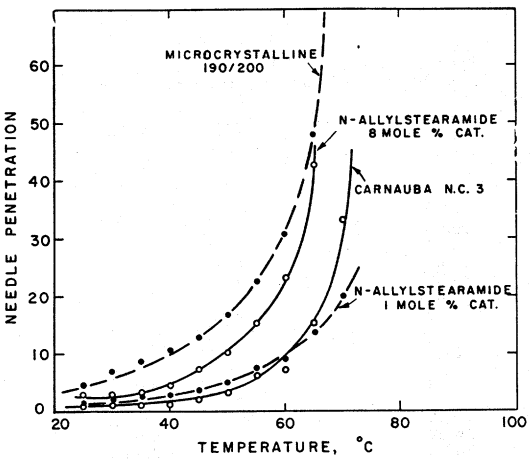

FIG. 2. Variation of needle penetration number with temperature for several waxes.

certain commercial waxes (Expts. 15, 17, 18) but was considerably inferior to polyethylene and the petroleum waxes. Color of the solid products varied from white at the lowest peroxide concentrations through light tan in the optimum region, to light brown at 12 mole % peroxide. Densities showed irregular variations not related in any apparent way to changes in crystal size.

The nature of the products formed in the allylstearamide system seems to be the cause of the morphological changes conferring wax properties. When unlike compounds, such as N-butylstearamide, methyl stearate, stearamide, and polyvinyl stearate were melted together with the pure tallow amide to make a mixture consisting of 10.63 g of additive per 100 g amide, macrocrystalline compounds were formed which had low Brinell hardness values of, respectively: 47.9, 42.9, 41.5, and 32.0. The bulk of the morphological changes in the allylamide system appeared to be caused by the accumulation of polyallylstearamide rather than by the presence of aromatic substitution products. Thus, when pure polyallylstearamide, isolated as in (10), was melted and mixed with monomeric N-allylstearamide (in the ratio of 9.71 g of polymer to 100 g amide) to produce a composition intermediate in polymer content to experiments 4 and 5, needle penetration was 1.1 and Shore hardness was 99.3. This indicated even greater hardness than was observed with the comparison experiment. Melting point (82.5–83.0C) was also a little higher, because the aromatic byproducts were missing.

The benzoic acid formed in the wax compositions (Table II) as a result of transfer reactions (10) was insoluble, and, in time, exuded to the surface causing a bloom to develop on the films, the amount developed being roughly proportional to the acid content. The presence of the acid had no apparent effect on the physical properties, however. Brinell hardness, run on samples from which the acid had been removed by extraction, was: 2 mole % peroxide, 145.3; 3 mole %, 164; 6 mole %, 171; 8 mole %, 169.6. Needle penetration was the same as when the samples were not extracted. Even at acid numbers <1, slight bloom still persisted on thin films.

The allylamide waxes were found to be compatible in 1:1 mixtures with the commercial waxes listed in Table IV except for polyethylene, with which compatibility was only found in 9:1 amide to polyethylene mixtures.

Resistance to oxidation was tested by exposing thin films of two waxes (Expt. 9, 14), and methyl oleate as a control to air at 90C for 96 hr. In methyl oleate percent active oxygen rose to 0.061 in 6.5 hr and was 0.66 at 72 hr, but in the amide waxes it remained at zero.

Iodine number of the amide remained unchanged. Thus, in spite of the presence of much unsaturation in the allylamide system, little oxidation apparently occurred.

Floor tests, covering a four-week period, on films made from wax pastes, prepared as described in the experimental section, were compared with films made from the following commercial waxes: carnauba N.C. No. 3, a modified Fischer-Tropsch wax (Duroxon J-324), methylene-bis-stearamide (Armowax), A-C polyethylene 629, and hydrogenated tallow. The allylamide films possessed high gloss, approaching the gloss of carnauba and Fischer-Tropsch wax and superior to the others. Wearing ability, while inferior to carnauba and the Fischer-Tropsch wax, was superior to that of the other waxes, especially during the first two weeks of testing. Repolishing characteristics were again inferior to the hard commercial waxes but were better than the others. In general, mechanical properties were a rough function of hardness.

Emulsions were prepared as described in the experimental section. Again no attempt at optimization of the arbitrary recipe was made. The emulsions of the mixed allylamides were poor, being thick and creamy and of fairly large particle size. The emulsions held without breaking, however, over extended periods. Floor tests on the emulsions paralleled in a rough way those of the pastes, but buffing was required in all cases. Further investigation would be required to eliminate the bloom and improve the quality of the emulsions for this system.

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