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 90°C for 3 hr with benzoyl peroxide, the reaction products were medium-hard, high-melting (ca. 70–80°C) 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 floor wear tests on films obtained from paste and emulsion compositions showed the allylamide waxes to be inferior to carnauba and a Fishertropsch wax, but superior to several other synthetic waxes including polyethylene. No special property advantage was found using pure allylstearamide. Resistance to oxidation at 90°C was good and the waxes emulsified readily.

In the reaction of allylstearamide with benzoyl peroxide, polymer formation depends strongly on catalyst concentration (d M/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), acrylies (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 90°C 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 allyl acetate. This results from an unfavorable competition for the benzoylperoxy 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.

\[
\begin{align*}
\text{CH}_2 = \text{CH} - \text{CH} - \text{NH} - \text{COR} & \quad \text{CH}_2 = \text{CH} - \text{CH} = \text{NH} - \text{COR} \\
& \quad \text{CH}_2 = \text{CH} - \text{NH} - \text{COR} \quad \text{C} = \text{O}
\end{align*}
\]

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 (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 70°C 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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twice from acetone (10 ml/g) at 0°C. Results were:

Pure N-allylstearamide: yield 85.3%; mp 83.8–84.3°C;
ester No. 0.0; % carbon, calcd. 77.98, found 77.61; %
hydrogen, calcd. 12.77, found 12.70; % nitrogen, calced.
4.33, found 4.31. Mixed tallow amides: yield 75.6%;
mp 75.0–79.0°C; ester No. 0.0; % carbon, calcd. 77.71,
found 77.99; % hydrogen, calded. 12.72, found 12.91,
% nitrogen, calded. 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 90°C 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 60°C, 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
after the addition of the last increment of the
peroxide, to complete consumption of the initiator.
Unextracted, the crude reaction mixture was
poured into appropriate molds for testing.

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 allylamine 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. Be-
cause the solubilities of the allylstearamide waxes,