

Epoxidized Esters of Fatty Acids as Internal and External Plasticizers for Polyvinyl Acetate¹

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A GROWING MARKET has been developing for polyvinyl acetate emulsions as a component of water-base paints. The wide use of these emulsions is attributed to the availability of their components, low cost, ease of formulation, ease of application in painting, and the resistance of the film to degradation by sunlight. However fusion of the drying latex⁴ to form a uniform film at the usual ambient temperatures encountered in outdoor painting fails to occur unless the polyvinyl acetate has been modified. In one method of modification, external plasticizers (liquids compatible with polyvinyl acetate and having high boiling points) are added to the latex. These liquids function by lowering the fusion temperature of the film. The most widely used external plasticizers belong to the general class of esters, of which the esters of dibasic acids and of phosphoric acid are the most important commercially. Simple glycerides and other monobasic fatty acid esters are unfortunately incompatible with polyvinyl acetate, thereby limiting their use as polymer modifiers (5).

In an alternate modification technique (internal plasticization), copolymers of vinyl acetate having lower fusion temperatures than polyvinyl acetate are used in its place. As co-monomers for internal plasticization, alkyl acrylates (8), chloroprene (8), and vinyl esters of long-chain fatty acids (6) have been reported.

As part of a general program of this laboratory for discovering new uses and applications for fats, an investigation was undertaken on the modification of fatty acid esters to produce plasticizers for polyvinyl acetate. This paper describes the use of esters of epoxy, hydroxy-acetoxy, and polyacetoxystearic acids as external plasticizers for polyvinyl acetate latex and the preparation of emulsions of copolymers of vinyl acetate and vinyl epoxystearate. The role of the epoxy group as an acetic acid scavenger (2, 4) under emulsion conditions was also investigated. Such scavenging action is desirable to prevent container corrosion and to promote emulsion stability.

Experimental and Results

Materials. Vinyl acetate obtained from a commercial source was fractionally distilled before use. The fraction boiling at 72°C. was used in this investigation. Vinyl epoxystearate was prepared by the method of Silbert *et al.* (7). The esters studied were epoxidized soybean oil (ADMEX 710,⁵ oxirane oxygen, 5.87%) from Archer-Daniels-Midland Company; butyl epoxystearate (Estynox 403, oxirane oxygen 4.02%), butyl hydroxy-acetoxystearate (Estynox 203), and butyl polyacetoxystearate (Estynox

206) from the Baker Castor Oil Company. Acetostearin (acetyl stearyl glycerides) and aceto-olein (acetyl oleyl glycerides), prepared from soybean oil, were obtained from the Southern Regional Research Laboratory. These oils were used without further purification.

A mixture of acetyl epoxystearyl glycerides (oxirane oxygen 4.50%) was prepared by direct epoxidation of aceto-olein by the method of Findley *et al.* (2). 2-Methoxyethyl 9,10-epoxystearate was prepared by the epoxidation of 2-methoxyethyl oleate, an ester obtained by the acid-catalyzed esterification of oleic acid with methyl cellosolve.

Sulfonated red oil, Pluronic F68,⁶ and Triton W-31,⁷ are commercial emulsifiers and were used without further purification. Reagent grade potassium persulfate was the polymerization initiator used.

Screening Tests. Proposed plasticizers were first screened for compatibility by preparing solutions of each ester with polyvinyl acetate in toluene and coating films from these solutions onto glass plates. The solutions, consisting of 90 g. toluene, 10 g. polyvinyl acetate, and 2.2 to 5.4 g. plasticizer, gave concentrations of plasticizer ranging from 18 to 35% in the plasticized polyvinyl acetate films after complete evaporation of the toluene solvent. After complete drying at room temperature, the films were examined for evidence of separation of the plasticizers. A plasticizer was considered to be compatible if the resulting film was clear and flexible and showed no separation of oil. The results of these tests are listed in Table I. All of the compounds studied except aceto-stearin and aceto-olein were compatible. It was found that the limit of compatibility was attained when approximately 20% of plasticizer had been added to the polymer. Although the epoxy compounds were compatible with polyvinyl acetate, they would be of limited utility if the products of their reaction with acetic acid were found to be incompatible.

Consequently compatibility observed for butyl hydroxy-acetoxystearate (Table I), arising as a product of the butyl epoxystearate-acetic acid reaction, demonstrated that the use of butyl epoxystearate as a plasticizer would be practical.

Preparation of Plasticized Polyvinyl Acetate Emulsions. It remained to be demonstrated that the plasticizers listed in Table I could be added to an emulsion of polyvinyl acetate to form a latex from which a plasticized film could be cast.

A useful formulation for the preparation of a polyvinyl acetate latex is given in Table II. Vinyl acetate was added with rapid stirring to an oxygen-free solution of Pluronic F68, sulfonated red oil or Triton W-31, and potassium persulfate (0.55 g.), reserving 12 ml. of water for the gelatin and additional potassium persulfate. The mixture was heated under nitrogen for 1.5 hrs. at 64°, and 6 ml. of a solution

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⁴ A latex is defined as an aqueous dispersion of colloidal polymer particles which has been stabilized by an emulsifier.

⁵ Reference to commercial products in this publication is not intended to be a recommendation of these products by the U. S. Department of Agriculture over others not mentioned.

⁶ A condensate of ethylene oxide with a hydrophobic base formed by condensing propylene oxide with propylene glycol.

⁷ Sodium salt of an alkylaryl polyether sulfate.

TABLE I
Compatibility of Modified Fatty Acid Esters with Polyvinyl Acetate

Plasticizers ^a	Compatibility
Acetyl epoxystearyl glycerides.....	Compatible (slightly tacky)
Epoxidized soybean oil.....	Compatible
Butyl epoxystearate.....	Compatible
Butyl hydroxy-acetoxystearate.....	Compatible
Butyl polyacetoxystearate.....	Compatible
2-Methoxyethyl 9,10-epoxystearate.....	Compatible
Aceto-stearin.....	Incompatible
Aceto-olein.....	Incompatible

^a 18% plasticizer concentration in the plasticized polyvinyl acetate film.

TABLE II
Recipe for Polyvinyl Acetate Latex

Vinyl acetate.....	100.0 g.
Pluronic F68 (100% basis).....	4.5
Sulfonated red oil (100% basis) ^a	3.0
Water.....	142.0
Potassium persulfate.....	0.75
Gelatin.....	0.38

Triton W-31 may be substituted.

containing gelatin (0.08 g.) and potassium persulfate (0.20 g.) were added dropwise. The polymerization was permitted to proceed for one hour at 64°, then raised to 75° for 10–15 min. to complete the reaction. The emulsion was rapidly cooled and filtered through a fine-mesh screen to remove small quantities of coagulum and foam; and the remainder of the gelatin dissolved in 6 ml. of water was added to enhance stabilization. Addition of methanol (about 1% by weight), after one hour of polymerization, was also found useful for decreasing coagulum and foam during polymerization (9).

Polyvinyl acetate emulsions were post-compounded by slowly adding, with stirring, stable pre-emulsified epoxy and acetoxy oils, which were prepared in a high-speed blender in accordance with the recipe in Table III.

TABLE III
Recipe for Oil Plasticizer Emulsions

Fatty acid ester.....	25.0 g.
Pluronic F68.....	2.25
Sulfonated red oil ^a	1.5
Gelatin.....	0.2
Water.....	71.0

^a Triton W-31 may be substituted.

Sufficient oil-in-water emulsion was added to the polyvinyl acetate emulsion to give the desired concentration of plasticizer in the polymer film. The resulting emulsion was aged for two weeks at room temperature to permit migration of the oil into the polymer particles. Films cast on glass plates from these emulsions were examined for compatibility. Compatibility was obtained by this technique for 5 to 20% plasticizer combinations with butyl epoxystearate, butyl hydroxy-acetoxystearate, butyl polyacetoxystearate, and 2-methoxyethyl 9,10-epoxystearate, but not for epoxidized soybean oil or acetyl epoxystearyl glycerides. Dillon and coworkers (1) have shown that some low-molecular-weight solvents may aid in the plasticization of a polymer latex by increasing the rate of diffusion of the plasticizer. Therefore 0.4 part of toluene per part of epoxidized oil was added to the epoxidized soybean oil and to the acetyl epoxystearyl glycerides in a subsequent test. The use of toluene as a diffusion activator permitted complete plasticization by these epoxidized oils within 24 hrs.

Internally Plasticized Co-polymer Latex. Inter-

nally plasticized polyvinyl acetate emulsions, containing 5, 10, and 20% by weight of vinyl epoxystearate in the interpolymer, were prepared by co-polymerizing vinyl acetate with vinyl epoxystearate by the technique described by Port *et al.* (6). A preferred recipe for an 80:20 ratio by weight of vinyl acetate to vinyl epoxystearate is formulated in Table IV.

TABLE IV
Recipe for Vinyl Acetate-Vinyl Epoxystearate Latex

Vinyl acetate.....	80.0 g.
Vinyl epoxystearate.....	20.0
Water.....	142.0
Sulfonated red oil or Triton W-31.....	5.3
Pluronic F68.....	2.3
Potassium persulfate.....	0.60

The co-polymerization was conducted at 70° for three hours. Films cast from these emulsions were clear, flexible, and resistant to water and to abrasion. These films could be cross-linked to insoluble polymers by the addition of amines or dibasic acids to the emulsions.

Acetic Acid Scavenging Action of the Epoxy Group. After 95% conversion to polymer of these polyvinyl acetate emulsions, the remaining unreacted vinyl acetate hydrolyzes slowly at room temperature, producing acetic acid.

This acetic acid concentration was determined in the non-plasticized, co-polymerized (20% by weight of vinyl epoxystearate), and externally plasticized (15% by weight of epoxidized esters) emulsions. Five-milliliter samples were periodically pipetted, diluted with 50 ml. of water, and titrated with 0.1 *N* sodium hydroxide, using phenolphthalein indicator. Figure 1 indicates the change with time of the acetic acid concentration calculated as milligrams of acetic acid per 100-ml. emulsion; the data are plotted as a titration difference between the initial and successive samples. (The emulsions contained an initial acidity arising from hydrolysis of vinyl acetate during polymerization.)

Figure 1 illustrates the rapid accumulation of acetic acid for the non-plasticized (non-stabilized) emulsion compared to a slower accumulation for the emulsions containing external epoxy plasticizers (externally stabilized) or for the co-polymers (internally stabilized). The curves clearly demonstrate that the larger the concentration of oxirane oxygen in these emulsions, the smaller the increase in acetic acid.

A determination of the quantitative differences between the plasticized and non-plasticized emulsions was not undertaken in this investigation because of the large number of variables which would have to be determined. It was of interest however to determine whether accumulation of acetic acid could be prevented by using an excess of oxirane oxygen to vinyl acetate. For this study, emulsions of butyl epoxystearate-vinyl acetate (monomer) systems were prepared in accordance with the general recipe of Table III. The epoxy ester vinyl acetate ratios in the emulsions were adjusted to result in mole ratios of 1:2, 1:1, and 7:1. The 10-ml. samples were periodically pipetted for acid determination. The periodic change of acetic acid is represented in Figure 2.

A mole of vinyl acetate would be expected to produce two moles of acetic acid by hydrolysis to acetic acid and acetaldehyde with subsequent oxidation of the aldehyde. The curves for the 1:2 and 1:1 mole ratios of oxirane oxygen vinyl acetate therefore rep-

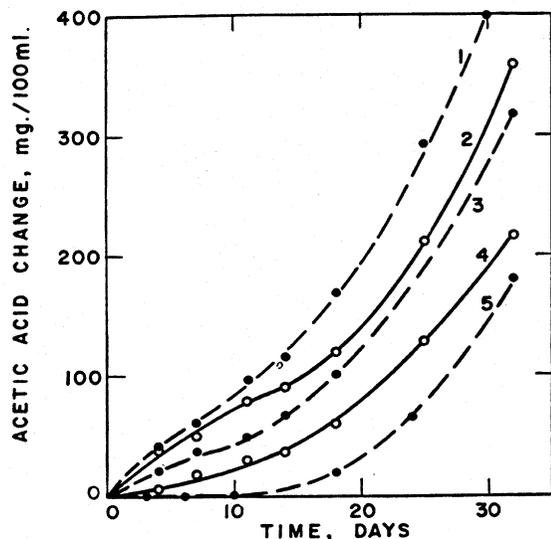


FIG. 1. Change in acetic acid content of plasticized and non-plasticized polyvinyl acetate emulsions containing 1.8% vinyl acetate.

1. Non-plasticized polyvinyl acetate emulsion.
2. Butyl epoxystearate; 0.21% oxirane oxygen.
3. Acetyl epoxystearyl glycerides; 0.23% oxirane oxygen.
4. Epoxidized soybean oil; 0.30% oxirane oxygen.
5. Vinyl acetate-vinyl epoxystearate copolymer (80:20 mole ratio); 0.38% oxirane oxygen.

represent an excess of potential acetic acid. Accordingly an expected accumulation of acetic acid was observed. The 7:1 curve represents a three-fold excess of oxirane to potential acetic acid. The acetic acid content of this emulsion initially decreased, followed by a slow increase in acid content. Thus the presence of an excess of oxirane did not prevent an accumulation of acetic acid. This unexpected increase in acid suggests that the reaction may be more complex than the simple addition of acetic acid to the oxirane group.

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Summary

Fatty acid esters modified with epoxy or acetoxy groups were found to be compatible with polyvinyl acetate. These esters are good plasticizers for polyvinyl acetate compositions and may be used for plasticizing polyvinyl acetate in latex form. The use of a good swelling agent, such as toluene, was found desirable for permitting plasticization of these

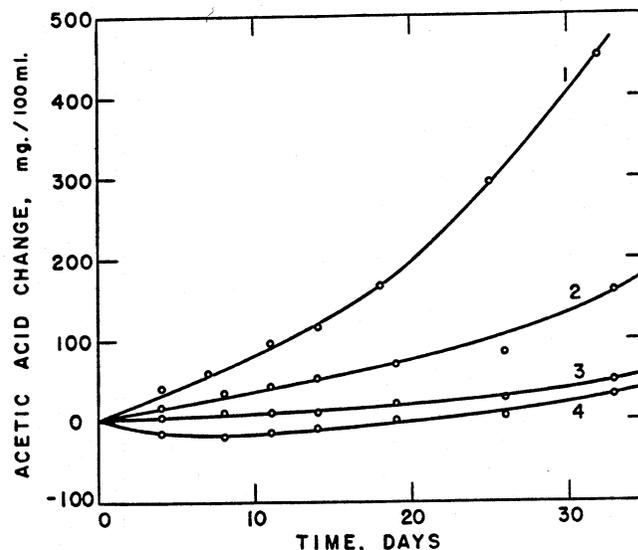


FIG. 2. Change in acetic acid content of butyl epoxystearate-vinyl acetate (monomer) emulsions.

1. No plasticizer; 1.8% vinyl acetate.
2. Mole ratio of oxirane oxygen to vinyl acetate 1:2; 2.7% vinyl acetate.
3. Mole ratio of oxirane oxygen to vinyl acetate 1:1; 1.3% vinyl acetate.
4. Mole ratio of oxirane oxygen to vinyl acetate 7:1; 1.3% vinyl acetate.

emulsions. The epoxidized oils may also assist in reducing container corrosion and in stabilizing the emulsions by reacting with the acetic acid formed by the hydrolysis of residual vinyl acetate.

Emulsions of copolymers of vinyl acetate and vinyl epoxystearate were prepared, yielding clear, hard films which were internally plasticized. The epoxy group in these interpolymers is a potential source for cross-linking vinyl acetate polymer films. The epoxy group of the co-polymers (internal-phase stabilization) and the epoxidized oils (external-phase stabilization) were found to be virtually equivalent for removal of acetic acid from polyvinyl acetate emulsions.

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