

# **Influence of Emulsifiers on Film Formation from Cellulose Acetate Latexes Experimental Study of Phase Separation Phenomena Due to Sodium Dodecyl Sulfate. I.**

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## **Synopsis**

Cellulose acetate membranes prepared from latexes containing sodium dodecyl sulfate as a stabilizer were found to undergo phase separation. This phenomenon was studied by different techniques including autoradiography, optical and scanning electron microscopy, mechanical testing, and liquid water permeation. The concentration of sodium dodecyl sulfate in the dry membranes was found essential in controlling their structure and properties, as well as the nature and amount of plasticizer incorporated in the latex system. The method of preparation and the drying duration were also relevant. Depending on whether films were produced by casting or spraying, tensile and permeation values exhibited quite different responses to variations of the sodium dodecyl sulfate content. In Paper II, a thermodynamic framework is proposed that accounts for the redistribution of sodium dodecyl sulfate into small islets, and thus for phase separation.

## **INTRODUCTION**

### **General**

In the pharmaceutical field, the need to phase out organic solvent film coating offers an incentive to develop latex systems. In recent years, ethylcellulose (Aquacoat FMC) and cellulose acetophthalate (Aquateric FMC) latexes have appeared on the market, produced by a technique of direct emulsification of the polymer.<sup>1-3</sup>

We have extended this procedure to manufacture cellulose acetate latexes with a typical particle size in the range of 100 nm to 1  $\mu\text{m}$ .<sup>4,5</sup> Basically, these aqueous dispersions were prepared by dissolving the polymer in an appropriate solvent and dispersing the solution in an aqueous phase containing surfactants as emulsion stabilizers. The outcoming crude emulsions were then passed through a valved high-pressure homogenizer, and the solvent was finally evaporated under reduced pressure. A potential important application of such latex systems is to produce coatings for elementary osmotic pumps, a class of pharmaceutical devices for controlled drug delivery.<sup>5,6</sup>

The supermolecular structure of membranes prepared by casting organic solutions of polymer is dictated, at least to some extent, by the thermodynamic interaction between the solvent and the polymer molecules, or in other instances between the plasticizer and the polymer.<sup>7-15</sup> In contrast, such a

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simple situation does not necessarily exist for latex films, since latexes usually contain one or several emulsifiers which prevent coagulation of the particles and remain in the final films. Although they are needed, these emulsifiers may strongly impair the film properties and structure, and therefore the nature and concentration of surfactants entering the composition of a latex should not be ignored at the stage of its utilization.

In this two-part series, we attempt to throw some light on the connections between film structure and emulsifier properties. After a survey and critical analysis of previous work on the fate of emulsifiers, we show in part I that phase separation phenomena are manifest in cellulose acetate membranes prepared from latexes containing sodium dodecyl sulfate together with water-soluble plasticizers. Various concentrations of SDS were tested, falling within a range suitable for latex production. In part II,<sup>16</sup> we propose a thermodynamic framework to account for the demixing phenomena observed. We also suggest a few guidelines for the selection of appropriate surfactants.

#### Literature survey on the fate of emulsifiers in latex films.

About 30 years ago, Wheeler et al.<sup>17</sup> noticed that films cast from poly(vinyl acetate) latexes had a marked tendency to whiten and to disintegrate in contact with water, even after several years storage. This property was attributed to poly(vinyl alcohol), an emulsifier that seemed to form an interface between the particles and hinder their coalescence. From crosslinking experiments, these authors<sup>17</sup> concluded further that the mechanical strength of the films was impaired by emulsifiers immobilized at the surface of the particles. They suggested that additives such as gum arabic, which they believed were incompatible with poly(vinyl acetate), should be preferred since they were readily displaced from the interface into islets.

Voyutskii<sup>18</sup> stated that emulsifiers were likely either to dissolve in the polymer (plasticizing effect) or remain in the film as an independent network. According to this worker,<sup>18</sup> only the appearance of such a network could explain the ability of rubber films to swell and, at the same time, their failure to redisperse. From tensile testing of vulcanized and unvulcanized rubber films, Voyutskii et al.<sup>19,20</sup> deduced that the films of the latter class were probably ruptured in the rubber substance of the particles themselves rather than along the very strong protein interlayers between the particles or at the protein-rubber interface (proteins act as natural stabilizers in rubber latexes). Thus, it was established that an emulsifier network did not necessarily result in weak films, but could act in some instances as an interparticulate cement. Furthermore, the strength of vulcanized films was found to depend on their degree of swelling in water vapor or petrolatum, as well as on the temperature. This corroborated the idea that the strength of these films is caused mainly by Van der Waals forces between the particles. A similar conclusion was reached by Eliseeva and Chubareva,<sup>21</sup> who found that adding ammonium caseinate improved the strength of various polyacrylate membranes, due to dipole-dipole interaction.

The work of Bondy and Coleman<sup>22</sup> roughly confirmed Voyutskii's assumption. A distinction was established between low-molecular-weight surfactants and hydrophilic colloid stabilizers, according to which the first class of emulsifiers had to be displaced from the surface of the particles for chain interdiffusion and coalescence to occur. In contrast, the macromolecules re-

mained adsorbed onto the globules, preventing their fusion but acting as a glue.

More direct experimental evidence about interstitial networks of emulsifiers was provided by the light-scattering and electron microscope studies of Wilkes and Marchessault<sup>23</sup> and Coté et al.<sup>24</sup> Some photographs revealed particles embedded in a nearly continuous poly(vinyl alcohol) phase and interconnected by fibrillar attachments.

According to Talen and Hover,<sup>25</sup> poly(vinyl alcohol) does not modify the sintering of poly(vinyl acetate) particles, since the emulsifier exudates toward the surface of the films and concentrates in channels. As underlined by the authors themselves, this conclusion was in flagrant contradiction to that of Wheeler et al.<sup>17</sup>

The exudation of incompatible surfactants during aging of latex films was studied by Bradford and Vanderhoff.<sup>26-28</sup> Investigations were carried out with nonyl phenol-ethylene oxide adducts of varying chain length. The long-chain compounds, hydrophilic and incompatible with the styrene-butadiene copolymer, were found to exudate toward the film surface whereas the short-chain lipophilic molecules remained inside the films.<sup>27</sup> Jäckel<sup>29</sup> demonstrated by a technique of microtome slides that hydrophobic materials accumulated near the surface. Other interesting results on the fate of emulsifiers were reported by Isaacs<sup>30</sup> and Panich et al.<sup>31</sup>

In view of the broad diversity of works and conclusions discussed above, we offer the following recapitulative analysis:

1. There are five possibilities for the fate of emulsifiers in latex films: the emulsifier migrates and dissolves in the polymer; the emulsifier exudates toward the surface of the film; independent islets are created that may or not correspond the interstitial voids between the particles; there is formation of a more or less continuous network embedding the globules; the emulsifier remains adsorbed on the surface of the particles as a monolayer. The supposition of dissolution holds for surfactants compatible with the polymer, while the next three assumptions better describe instances of incompatibility. The last possibility can fit both situations.

2. From case to case, the emulsifier may weaken or strengthen the interparticle bonds.

3. Although often put forward, the concept of compatibility between a polymer and an emulsifier is confusing. For instance, the distinction made by Wheeler et al.<sup>17</sup> between compatible and incompatible emulsifiers (the first category remains at the interface between the particles while the second concentrates into islets) is not clear from a thermodynamic standpoint. One should be able to distinguish the problem of "bulk phase" compatibility of a pair of polymeric components (which can be studied using Flory-Huggins theory<sup>32</sup>) from questions related to the adsorption of macromolecules or surfactant molecules onto the surface of particles which are relevant rather to theories of steric stabilization<sup>33</sup> or adhesion.<sup>34</sup>

4. The effect of the plasticizer or of the residual water on the process of redistribution of the emulsifier has not been discussed.

5. The forces involved in the migration and segregation of the emulsifier have not been considered.

6. There is little experimental evidence thus far to favor any particular one of the above assumptions (point 1).

In this two-part series, we will determine which of these assumptions correctly describes the film-forming process from plasticized cellulose acetate latexes.

## EXPERIMENTAL

### Materials

Latexes were prepared from cellulose acetate (CA) with a degree of acetylation of 39.8% (CA 398-10, Eastman Kodak, Rochester, NY). Sodium dodecyl sulfate (SDS) 99% pure was purchased from Fluka, Buchs, Switzerland.

The plasticizers (glycerol 1,3-diacetate=diacetin, diethyl tartrate, ethylene glycol diacetate, ethylene glycol monoacetate, triethyl and trimethyl phosphates) were supplied by Fluka. Their degree of purity was at least 97%, except ethylene glycol monoacetate and diacetin which were technical grade chemicals and contained a high proportion of the fully acetylated components, ethylene glycol diacetate, and triacetin, respectively. Gas chromatography of technical grade monoacetate showed the following composition: ethylene glycol monoacetate (50%), ethylene glycol diacetate (46%), and ethylene glycol (4%).

### Film Preparation

#### *Cast Films with Different Amounts of Sodium Dodecyl Sulfate*

A cellulose acetate latex with a mean particle size of 350 nm and a polydispersity index of 3, as measured with the Coulter Nano-Sizer (Coulter Electronics Ltd., Harpendon, U.K.), and an SDS content of 0.5% by weight of polymer, was used.

The blends to be cast contained 160% plasticizer by weight of CA, except those with ethylene glycol monoacetate and diacetate (320%). The percentage of CA in the blends was 6.0%. In order to study the effect of the SDS content of the latex on the dried film structure, the total amount of surfactant was adjusted to 2.0, 3.5, or 5.0% by weight of CA, respectively, by adding SDS.

The order of incorporation of the components was found to be important to prevent coagulation problems. A predetermined amount of water was first added to the plasticizer and to the surfactant. The concentrated latex (usually 30–40% solids) was then slowly poured into the plasticizer solution while stirring.

The mixtures were cast on glass plates to which siliconized glass rings of 9.3 cm inner diameter were fitted. Each film contained approximately 0.50 g CA, corresponding to 8.33 g total mixture. The drying was effected in an air-stream oven (Salvis TSW 270-E, Lucerne, Switzerland) at a temperature of 60°C during 54 h.

It is important to note that the exceptionally high amount of plasticizer added to the latex is required by the physicochemical properties of CA. In particular, solutions of this material are known to be very viscous,<sup>35</sup> reflecting highly entangled chains. However, at the temperature of 60°C the major part of the plasticizer evaporates (residual plasticizer content: 3–35% by weight of

CA, as measured by extraction with water. This is why the films produced are not soft, but strong.

Films for autoradiography were prepared in a similar way. Labelled SDS ( $^{35}\text{S}$ ) supplied by Amersham International was added at the level of 100  $\mu\text{Ci/g}$  CA. As the activity of the batch was 139.0 mCi/g or equivalently 40.1 mCi/mmol, it was calculated that the addition of radioactive SDS did not significantly modify the concentration of surfactant in the casting blends. To obtain thin films, the percentage of CA in the mixtures was reduced to 2.8%, the amount of water being adjusted in consequence. The blends were cast in Petri dishes of 9.7 or 14.5 cm diameter, each containing 0.25 g CA. Thicker films (0.5 g CA) cast in 9.7 cm dishes were also prepared. The drying was performed (air-stream oven) at 60°C during at least 96 h.

#### *Cast Films with Different Initial Amounts of Plasticizer*

The latex used here contained 3.75% SDS by weight of CA and the mean particle size was 230 nm, the polydispersity index being equal to 3. The casting procedure was similar to that described previously, except for the amount of plasticizer initially incorporated in the latex which was lower (60, 80, and 120%, respectively) and the drying duration (24 h at 60°C).

#### *Films Prepared by Spraying a Latex onto Potassium Chloride Disks.*

The aim of these trials was to obtain planar membranes in a similar way to that normally employed in coating techniques, i.e., by a fast evaporation process. These membranes of 20 mm diameter were obtained by a procedure described in more detail elsewhere.<sup>36</sup> Briefly, 80 g potassium disks of 20 mm diameter, prepared by direct compression of potassium chloride crystals (Siegfried, Zofingen, Switzerland) were mixed with 190 g small tablets (8 mm diameter) of microcrystalline cellulose (Avicel PH-101, FMC) in a fluidized bed column (Aeromatic Ktre-1, Muttentz, Switzerland). The disks of potassium chloride were heavy (2 g) but were maintained in suspension due to the light tablets. The flow rate of air was kept equal to 130 m<sup>3</sup>/h and the spraying air pressure was fixed at 1.5 kg/cm<sup>2</sup>. The exhaust air temperature was maintained at 65°C during the spraying. The sprayed latex systems contained 320% ethylene glycol monoacetate by weight of CA and various amounts of SDS (0.5, 2.6, and 5.0% by weight of CA, respectively). The latex containing 0.5% SDS had a mean particle size of 334 nm and polydispersity index of 3. For latexes with 2.6 and 5.0% SDS, these two parameters were equal to 277 nm and 3, respectively. The plasticizer was added as before (first subsection), but the concentration of CA in the spraying liquid was 7.35%. The rate of supply of coating liquid was 6.0 mL/min. The thickness of the coatings detached from potassium chloride disks was in the range of 200–300  $\mu\text{m}$ .

#### **Mechanical Properties**

Cast films were submitted to elongation trials using an Instron tester 1114 (Instron, High Wycombe, Bucks, U.K.). The samples were cut in rectangles

(length 76 mm; width 26 mm; thickness 30–150  $\mu\text{m}$ ), the distance between the grips was 51 mm, and the elongation rate was 0.1 mm/min.

Sprayed films were detached from their substrate, cut out in microtest pieces, and tested (Instron 1122) as reported elsewhere.<sup>5,37</sup> All samples were analyzed in triplicate.

### Water Permeability

The mechanical permeability  $L_p$ <sup>5,6,38</sup> of films prepared either by casting or spraying was measured at 37°C with a bicompartamental osmosis cell.<sup>36</sup> One chamber was filled with pure water, and the other with a saturated solution of potassium chloride. The transmembrane osmotically driven flux of water was measured by monitoring the level of liquid in a capillary pipette. Samples were analyzed in triplicate.

### Autoradiography

The films were inserted between two glass plates covered with a layer of photosensitive gelatine (Kodak fine grain autoradiographic stripping plates AR-10) and held together with clamps. The plates were left for 10 days in the dark before processing (developer Kodak D-19). They were finally examined and photographed with a Zeiss Ultraphot microscope.

### Sodium Fluorescein Assay

Films were soaked during 24 h in a 1% aqueous solution of sodium fluorescein (Siegfried, Switzerland), washed and immersed in water for 1 h, and dried in the air. The dry samples were then examined under a fluorescence microscope (Zeiss Ultraphot).

## RESULTS AND DISCUSSION

The effect on the film properties of their sodium dodecyl sulfate (SDS) content is examined with the six following techniques: optical microscopy, soaking with a sodium fluorescein solution, autoradiography, scanning electron microscopy, tensile testing, and water permeability measurements.

### Structure of Cast Films

#### *Optical Microscopy*

Figure 1 shows the effect of the amount of SDS on the structure of CA films with various plasticizers. One observes the appearance of opaque formations or of ridges. This heterogeneous structure appears after several hours drying, when the plasticizer has partially evaporated. This phenomenon cannot be seen with an SDS content of 0.5%, but becomes more and more obvious when the emulsifier content shifts from 2 to 5%.

After soaking in water and drying, films displaying phase separation phenomena become translucent or white (Fig. 2). Examination under a light

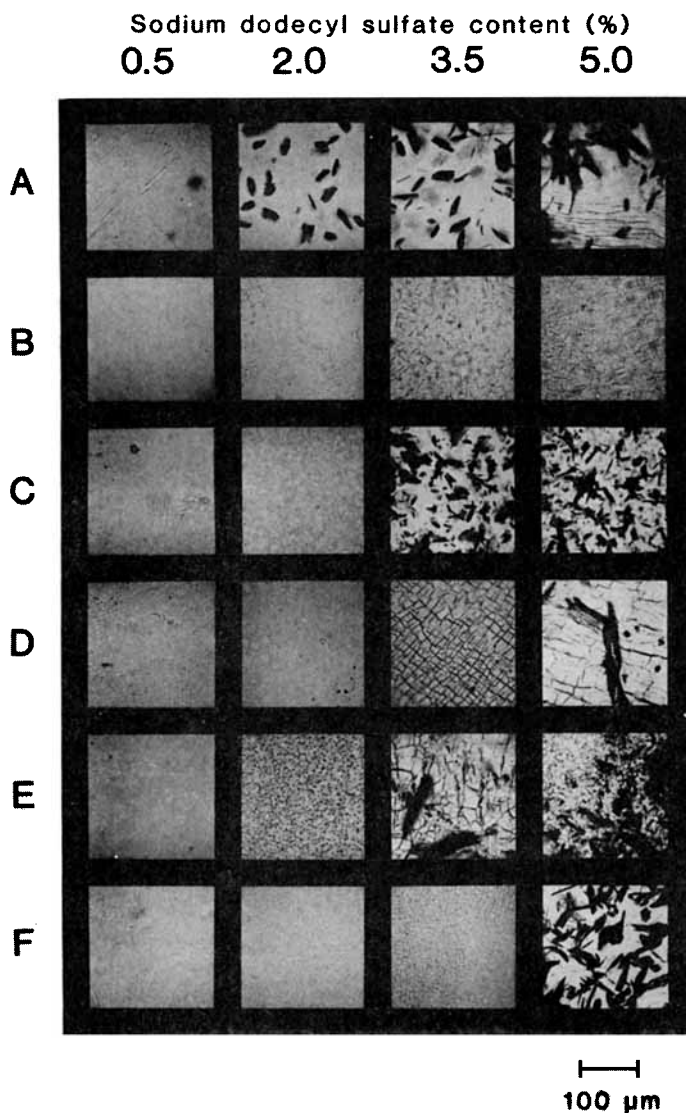


Fig. 1. Optical micrographs showing the effects of different plasticizers and of sodium dodecyl sulfate content on film structure: (A) diacetin (160%); (B) diethyl tartrate (160%); (C) ethylene glycol diacetate (320%); (D) ethylene glycol monoacetate (320%); (E) triethyl phosphate (160%); (F) trimethyl phosphate (160%). In brackets: initial amount of plasticizer in the latex.

microscope shows dark domains of well-defined shape. On the other hand, films containing only 0.5% SDS remain transparent after contact with water. As this behavior is observed whatever the water-miscible plasticizer is, e.g., for diacetin, ethylene glycol monoacetate, diethyl tartrate and triethyl and trimethyl phosphates, the opaque domains may be assumed to result from accumulation of SDS in some areas. When exposed to water, this surfactant is washed out and the formation of voids or pores may occur that scatter the light.

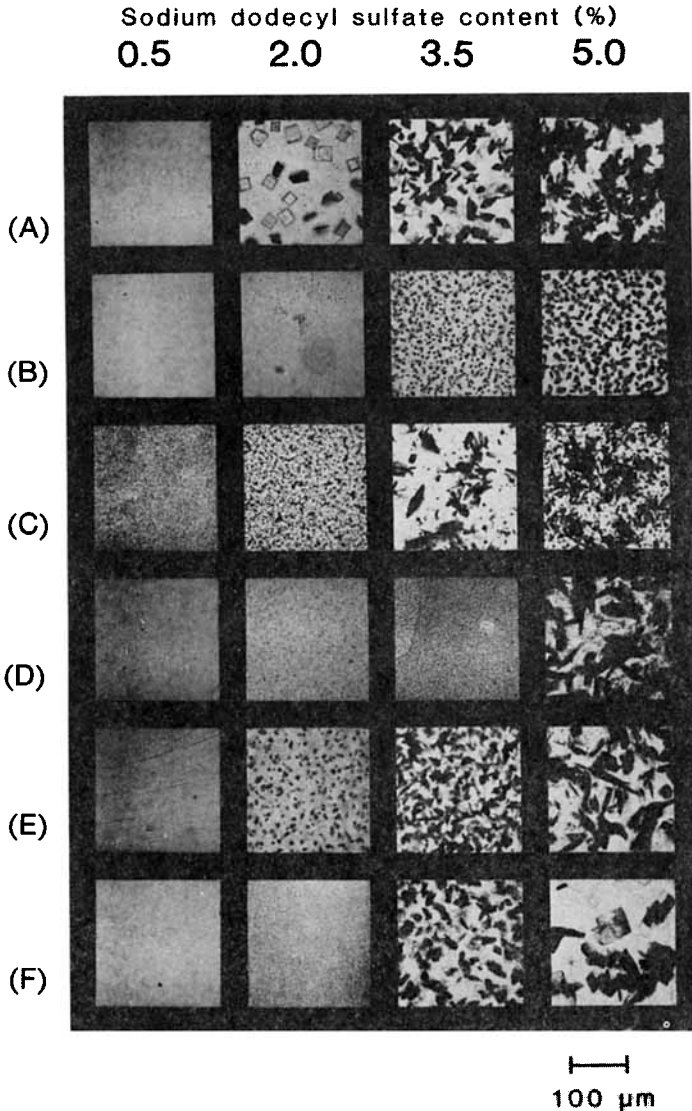


Fig. 2. Optical micrographs of dry films that have been exposed to water, showing the effects of different plasticizers and of sodium dodecyl sulfate content on film structure: (A) diacetin (160%); (B) diethyl tartrate (160%); (C) ethylene glycol diacetate (320%); (D) ethylene glycol monoacetate (320%); (E) triethyl phosphate (160%); (F) trimethyl phosphate (160%). In brackets: initial amount of plasticizer in the latex.

A further observation is that the shape, size, and number of dark islets are dependent upon the nature of the plasticizer (see Figs. 1 and 2) and its initial proportion in the casting latex (see Fig. 3). When the amount of plasticizer is low (60%), the islets are very small but numerous. On the contrary, they are disseminated yet large (several tenths or hundredths of microns) when the initial concentration of plasticizer is high (120% or more). After washing with



Initial amount of plasticizer in the latex (% by weight of CA)

60

80

120

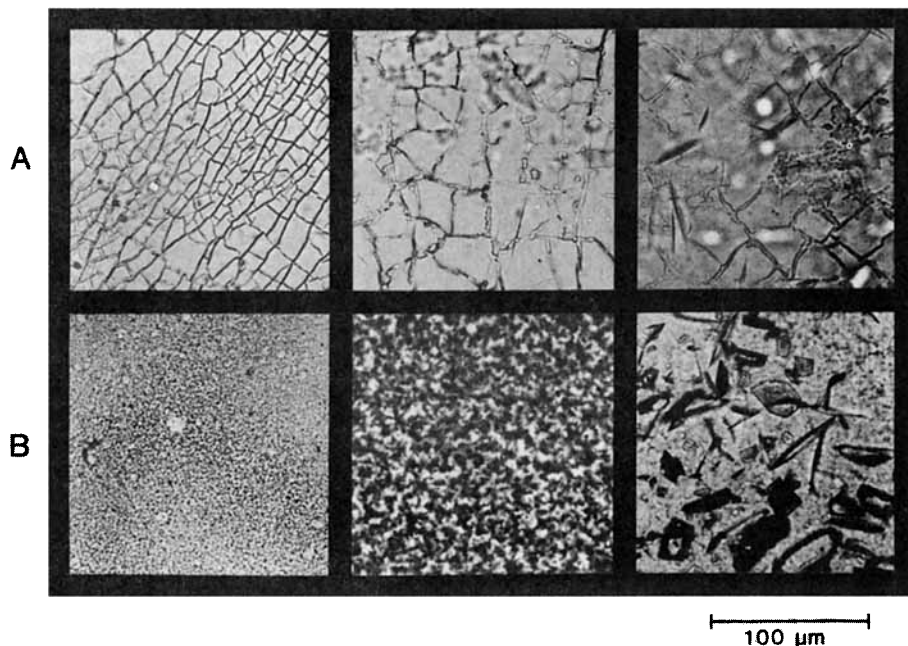


Fig. 3. Optical micrographs showing the effect of the amount of trimethyl phosphate added to the casting blends on film structure. Sodium dodecyl sulfate content: 3.75%. (A) Before washing; (B) after exposure to water and drying.

Sodium dodecyl sulfate content (%)

0.5

2.0

3.5

5.0

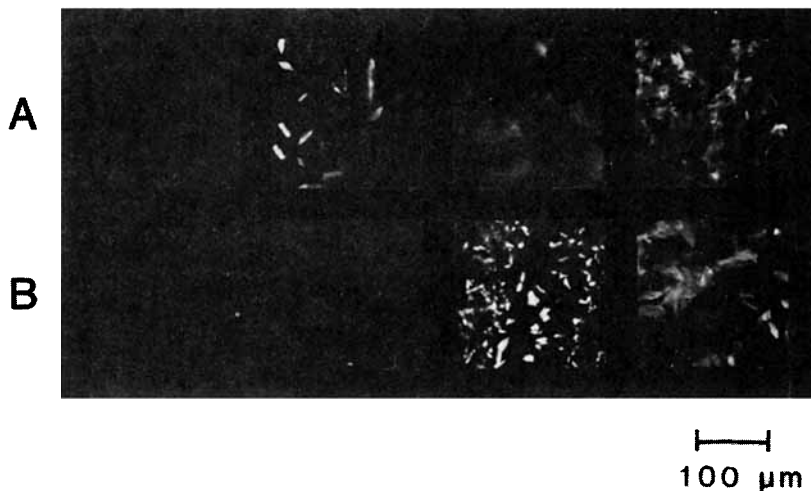


Fig. 4. Fluorescence optical micrographs showing unequal distribution of sodium fluorescein within films that contained various amounts of sodium dodecyl sulfate before washing: (A) diacetin (160%); (B) triethyl phosphate (160%). In brackets: initial amount of plasticizer in the latex.

water, the weakly plasticized films appear as uniformly white, while the membranes resulting from the evaporation of a highly plasticized blend remain spangled.

#### *Fluorescein Assay*

The presence of islets containing a high concentration of surfactant seems to be confirmed by a soaking test based on sodium fluorescein. This dye was found to be unable to penetrate into CA films obtained by casting acetic solutions, due to the dense and homogeneous character of this sort of films. Comparatively, membranes of apparently low density of macromolecular entanglements (such as highly plasticized films cast from an organic solvent) kept a certain coloration even after prolonged washing with water. Figure 4 illustrates this phenomenon for latex films containing diacetin or ethylene glycol monoacetate. Heterogeneous membranes exhibit fluorescent spots, shaped like the dark domains in Figure 2. This observation suggests that fluorescein penetrates into the pores created by the elution of SDS. In contrast, films with 0.5% SDS or less are not fluorescent.

#### *Autoradiography*

Autoradiography provides better confirmation of the unequal distribution of SDS than the simple criterion of heterogeneity. Indeed, the opaque domains in Figures 1-3 could be identified as simple cracks, if one supposes the

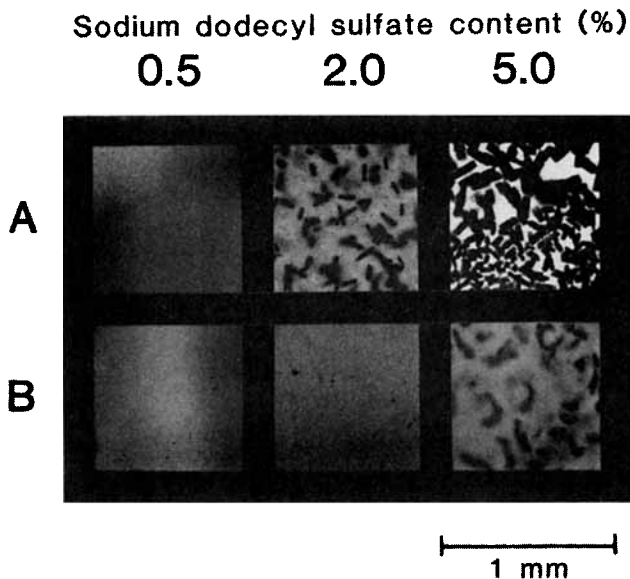


Fig. 5. Autoradiographs showing the effects of the nature of the plasticizer and of sodium dodecyl sulfate content on film structure: (A) diacetin (160%); (B) ethylene glycol monoacetate (320%). In brackets: initial amount of plasticizer in the latex.

cracking process to arise not from the accumulation of SDS in some places but simply from localized stresses due to the presence of this surfactant.

Figure 5 shows clearly the redistribution of the radioactive SDS which has concentrated during the film-forming process into small islets. On the contrary, the homogeneity of films containing 0.5% SDS is again apparent. In this case, the sensitive gelatin layer displays at the most large areas (several mm<sup>2</sup> or cm<sup>2</sup>) with poorly defined contours.

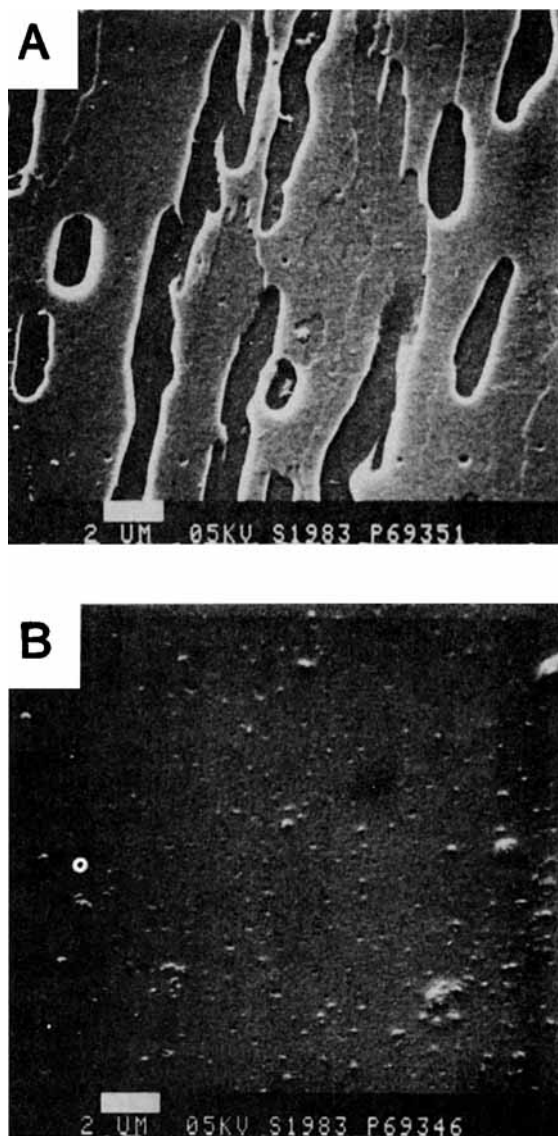


Fig. 6. Scanning electron micrographs showing the effect of sodium dodecyl sulfate content on film structure. All the films were plasticized with diacetin (initial amount in the latex: 160% by weight of cellulose acetate) and were washed with water. Sodium dodecyl sulfate content: (A) 5.0%; (B) 0.5%.

*Scanning Electron Microscopy*

Figure 6 refers to films plasticized with diacetin which have been immersed in water and dried. The effect of SDS on film structure is again visible. Membranes with 5% SDS [Fig. 6(A)] exhibit a network of channels or cracks which probably contained SDS prior to soaking in water [compare the 2% SDS formulations in Figs. 5 and 6(A)]. These cracks do not result from a defective welding between the particles, since the shape of the latter cannot be distinguished. Figure 6(B) is again a proof of the homogeneous character of membranes with 0.5% SDS.

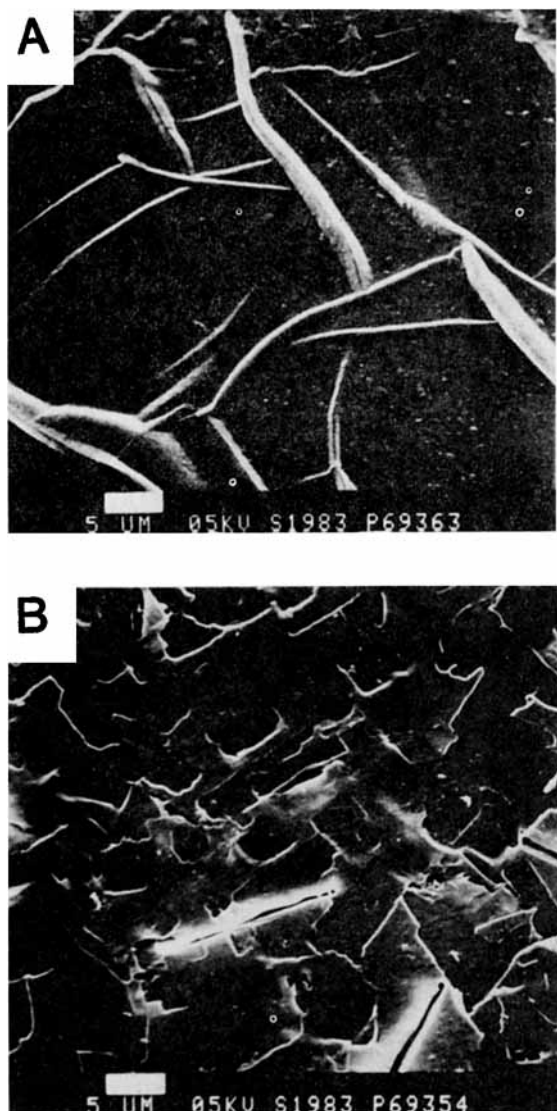


Fig. 7. Scanning electron micrographs of films plasticized with trimethyl phosphate (160% by weight of cellulose acetate) and containing 5% sodium dodecyl sulfate: (A) before washing; (B) after exposure to water and drying.

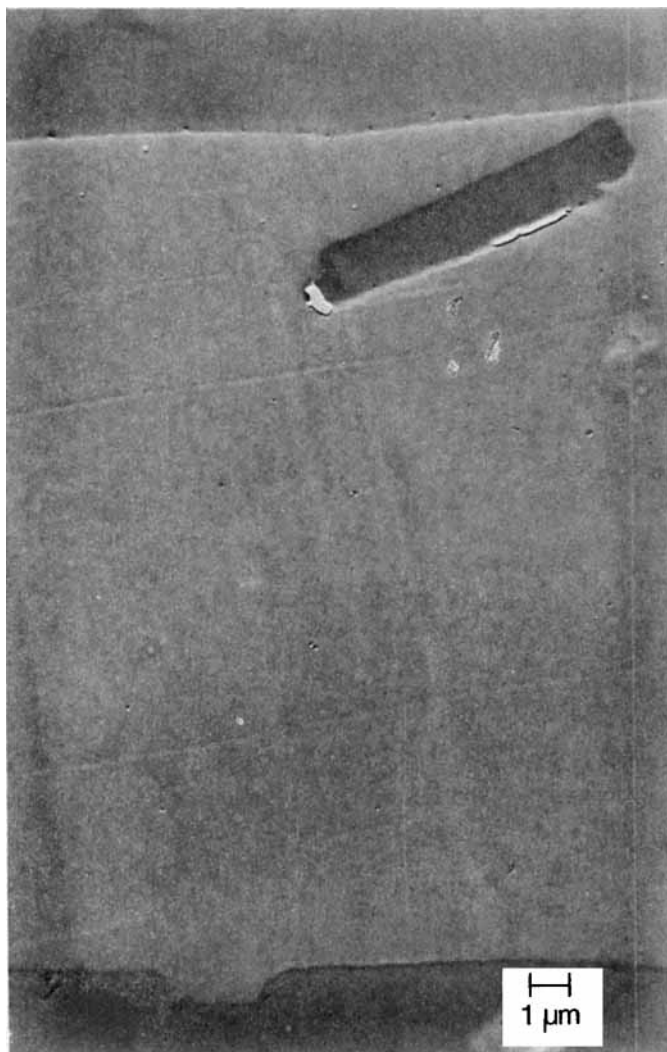


Fig. 8. Scanning electron micrographs showing the cross section of a membrane plasticized with diacetin and containing 2% sodium dodecyl sulfate. Initial amount of diacetin in the latex: 160% by weight of cellulose acetate.

Figure 7(A) corresponds to a film plasticized with triethyl phosphate before immersion in water. One notices a network of ribs which probably arise from exudation of SDS (compare with Fig. 3). This structure disappears after rubbing with a tissue or dipping in water and is, apparently, replaced by a system of channels [Fig. 7(B)].

Figure 8 shows the cross section of a membrane containing diacetin after washing in water. The asymmetric structure is apparent. Near the upper face, in contact with air during the drying, one can see large pores created by elution of the redistributed SDS. The lower face, in contact with the glass plate, is homogeneous.

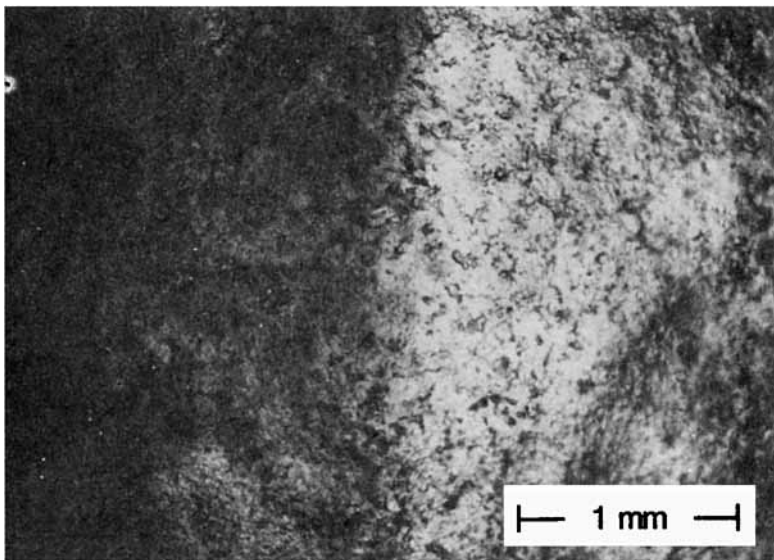


Fig. 9. Optical micrograph of a membrane prepared by spraying a latex onto potassium disks, after an elongation trial with an Instron tester. Sodium dodecyl sulfate content: 5.0%.

### Structure of Films Obtained by Spraying

In contrast with cast films, microscopic examination of sprayed membranes does not reveal the existence of opaque domains of geometrical aspect. To the eye, these films become uniformly white after exposure to water when they contain 2% SDS or more. A mechanical strain has the same effect as washing. Figure 9 shows a film, after an elongation trial, plasticized with ethylene glycol monoacetate (320% by weight of CA) and containing 5% SDS. The right end of the film, which was inserted in a grip, has remained unchanged whereas the left part displays phase separation, probably due to the appearance of anisotropic domains of submicroscopic size.

### Mechanical Properties

Figure 10 shows the variation of the ultimate tensile strength of cast films plasticized with various additives versus their SDS content. An increase of SDS results in a great decline of mechanical strength, whatever plasticizer is used. The same conclusion does not hold for membranes prepared by spraying. Figure 11 shows that the tensile strength of this kind of films is rather insensitive to its SDS content.

### Water Permeation

Cast formulations undergo an obvious increase of permeability after higher SDS loading (Fig. 12). Here, two volatile plasticizers were selected to obtain films with a low residual plasticizer content. Finally, Figure 13 shows that the

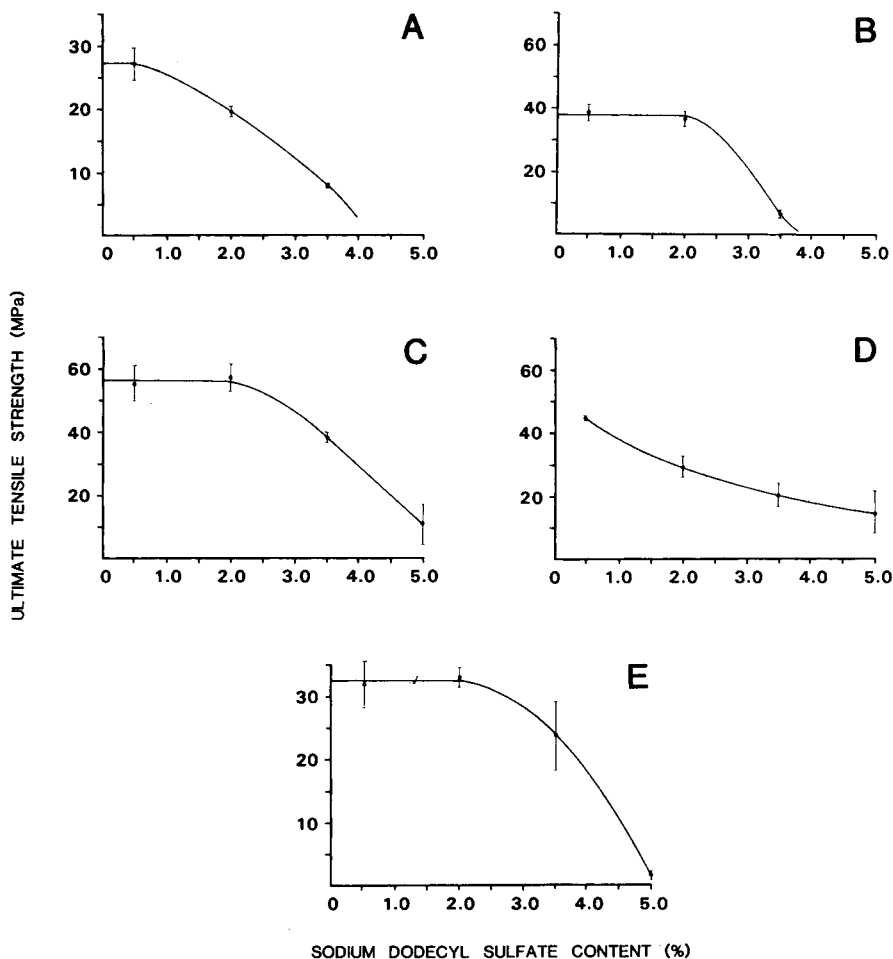


Fig. 10. Effect of sodium dodecyl sulfate content on the ultimate tensile strength of cast films plasticized with various additives. (A) diacetin (160%); (B) diethyl tartrate (160%); (C) ethylene glycol monoacetate (320%); (D) triethyl phosphate (160%); (E) trimethyl phosphate (160%). Data are expressed as mean  $\pm$ SDM.

permeability of films produced by spraying is very slightly affected by the percentage of SDS, in contrast with cast films.

## CONCLUSIONS

We have shown by different techniques including autoradiography that films prepared from cellulose acetate latexes undergo phase separation, due to SDS, an emulsifier entering their composition. With most plasticizers, this phenomenon was found to occur at an SDS content between 0.5 and 2.0%. This concentration range is normally encountered in CA latexes, and therefore much attention should be paid to this parameter, although phase separation was found less critical for films prepared by spraying.

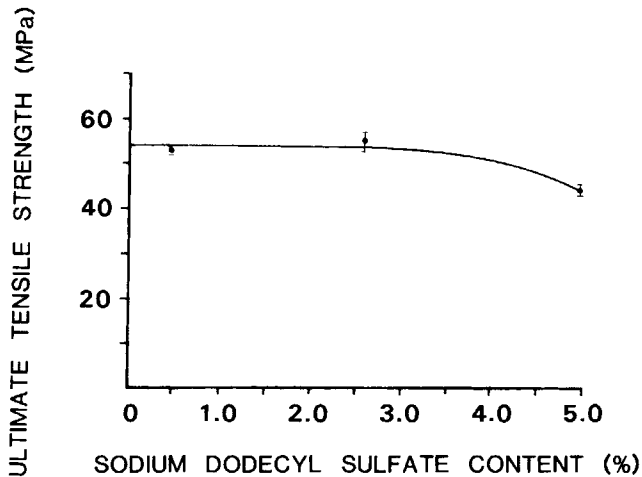


Fig. 11. Effect of sodium dodecyl sulfate content on the ultimate tensile strength of sprayed films plasticized with ethylene glycol monoacetate (320%). Data are expressed as mean  $\pm$  SDM.

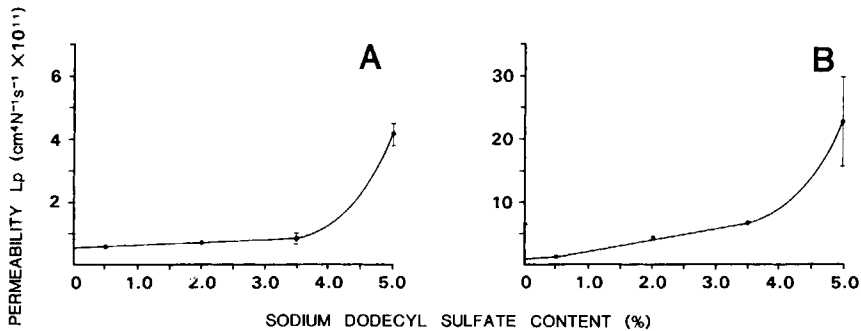


Fig. 12. Effect of sodium dodecyl sulfate content on the mechanical permeability of cast films plasticized with two different additives: (A) ethylene glycol monoacetate (320%); (B) triethyl phosphate (160%). Data are expressed as mean  $\pm$  SDM.

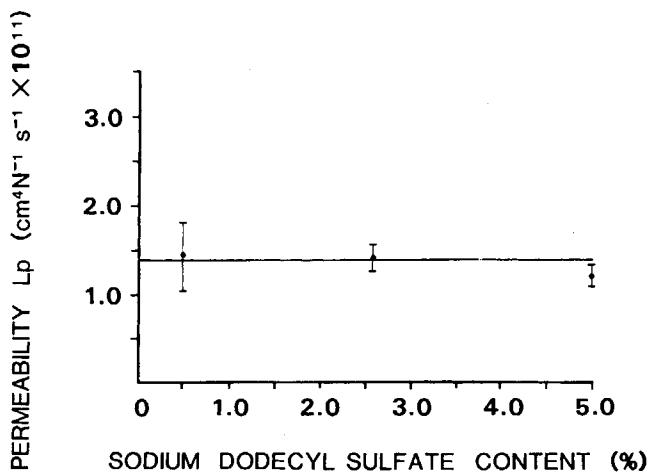


Fig. 13. Effect of sodium dodecyl sulfate content on the mechanical permeability of sprayed films plasticized with ethylene glycol monoacetate (320%). Data are expressed as mean  $\pm$  SDM.



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