JOURNAL OF APPLIED POLYMER SCIENCE VOL. V, ISSUE NO. 16, PAGES 491-492 (1961)

# The Effects of Sodium Salts on the Additive in Viscose Regeneration Process

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## INTRODUCTION

Some of the factors which influence the role of the additive in viscose were described in a previous paper.[1] The interdependence of the additive, the sulfur by-product, and zinc sulfate in reducing the degree of swelling of cellulose films and in retarding the rate of neutralization of viscose was demonstrated. However, some sodium salts were found to have a contrary effect in regard to gel swelling, and this effect is discussed in this paper.

## EXPERIMENTAL AND RESULTS

Equimolecular amounts of the sodium salts listed in Table I were added (0.1 mole/l.) to viscose which was prepared in the conventional manner with 8% cellulose and 6.5% sodium hydroxide (see details in the previous paper[1]). The ripened viscose was added to a vigorously stirred solution of Congo Red indicator. The sodium salt and the castor oil–polyethylene oxide additive were then added and the mixture stirred for one-half hour. Films prepared from the viscoses were coagulated and regenerated in a bath containing 7% sulfuric acid, 12.5% sodium sulfate, and 10.5% zinc sulfate. The rate of neutralization (the number of seconds required for the Congo Red indicator in the viscose to change from red to blue) was measured in the coagulating bath. In general, it was found that the addition of various sodium salts did not affect the rates of neutralization; the one exception, sodium sulfide, however, caused a delay in neutralization of viscoses with and without an additive.

A sample cut from the center portion of the coagulated film was blotted with absorbent pulp sheets, weighed, then washed free of bath acids and salts, and dried for 4 hr. at 100°C. The gel swelling factor was calculated from the ratio of the gel weight to the cellulose weight. The gel swelling ratio given in column 2 of Table I is the ratio between the gel swelling factors of the modified (additive + salt) cellulose film and the unmodified film.

## DISCUSSION

As was discussed previously, certain chemicals referred to as additives when used in viscose cause a reduction in gel swelling.[1] However, when sodium salts are introduced into the additive-containing viscose, a reverse effect is noted, and the effectiveness of the salts in swelling cellulose films follows a Hofmeister or lyotropic series: citrate > thiosulfate > tartrate > sulfate > chloride = phosphate = thiocyanate > acetate > nitrate > control = iodide > sulfide > carbonate.

High gel swelling ratios were obtained with the first nine members of this series when an additive was present in viscose; sodium iodide did not affect the usual deswelling of the films, and sodium sulfide and sodium carbonate caused the films to deswell slightly more than the control sample. In these additive-containing films, the changes in gel structure caused by the various salts were found to be permanent, i.e., after being washed free of bath acids and salts, and upon reswelling in water, the films retained their relative initial degree of swelling.

When the salts of the lyotropic series were added to the viscose without an additive, the gel swelling was essentially unaffected, i.e., the swelling ratios ranged from 0.9 to 1.1. The one important exception was sodium sulfide, which deswelled the cellulose to such an extent that the gel swelling ratio was lower than any value obtained for viscose with an additive.

The lyotropic series has been found to influence various colloidal phenomena and is apparently applicable to the degree of swelling of additive-containing viscose. It appears that the solvent

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TABLE I
Effects of Inorganic Salts on Viscose Films

| Sodium salts[a] | Gel swelling ratio: With additive | Gel swelling ratio: Without additive |
|---|---|---|
| Control (no salt added) | 0.52 | 1.0[b] |
| Citrate | 1.14 | 1.1 |
| Thiosulfate | 1.04 | 1.1 |
| Tartrate | 0.99 | 1.1 |
| Sulfate | 0.78 | 1.0 |
| Thiocyanate | 0.62 | 1.0 |
| Chloride | 0.62 | 1.0 |
| Phosphate | 0.62 | 1.0 |
| Acetate | 0.61 | — |
| Nitrate | 0.57 | — |
| Iodide | 0.52 | 0.9 |
| Sulfide | 0.5 | 0.42 |
| Carbonate | 0.47 | 0.9 |

[a] Added in the amount of 0.1 mole/l. viscose. At lower concentrations the relative effectiveness of the salts was the same but the various numerical values were grouped close together; at higher concentrations of salts the relative effectiveness was still the same, and in the additive-containing viscoses more exaggerated ratios were found.

[b] Swelling factor of unmodified control: 5.7.

molecules within the polymer network congregate around the ions of the added electrolyte, and the solvated salts interfere, in accordance with the lyotropic order, with the shrinkage of the film. The effects are more pronounced with viscose which contains an additive because the primary gel of the cellulose being regenerated is potentially more compact than the gel of films prepared from viscose without additives, and thereby it affects to a greater extent the movement of the electrolyte and water across the spin bath–viscose interface.

Our present experimental data are not adequate to explain the action of sodium sulfide, although on the basis of the mechanism of the deswelling of viscose gels proposed previously[1] one may speculate that the zinc ions of the spin bath which normally react with the xanthate to form zinc xanthate, and with the sulfur anions (sulfide, trithiocarbonate) to form zinc–sulfur derivatives, now have readily available an increased quantity of sulfide ions with which to form zinc sulfide. The precipitated zinc sulfide acts in a complex with itself or with zinc cellulose xanthate as a semipermeable membrane between the spin bath and the developing cellulose gel. This membrane, as discussed in Reference 1, controls the compactness of the gel structure and the diffusion of hydrogen ions.

The authors wish to express their appreciation to Dr. L. Skolnik for helpful discussions and to Mr. R. Sedlecky for measuring film properties.

## Reference

1. Levine, M., and R. H. Burroughs, *J. Appl. Polymer Sci.*, **2**, 192 (1959).

## Synopsis

Various chemical additives are commonly used in viscose to reduce the swelling of the resultant fibers and films. It was found that inorganic sodium salts, introduced into the additive-containing viscose, alter the action of the additive. The following salts, listed in order of the values of gel swelling ratios obtained with them, interfere with the deswelling of the viscose during regeneration: citrate > thiosulfate > tartrate > sulfate > chloride = phosphate = thiocyanate > acetate > nitrate > control. Sodium idodide did not affect the usual deswelling of the films, and sodium sulfide and sodium carbonate caused the films to deswell slightly more than the control sample. It was proposed that the effectiveness of the salts follows a Hofmeister or lyotropic series.

## Résumé

On emploie différents additifs chimiques dans la viscose afin de réduire le gonflement des fibres et films résultants. On a trouvé que les sels inorganiques de sodium introduits dans la viscose contenant l'additif changent l'action de l'additif. Les sels suivants, notés suivant l'ordre de leurs valeurs d'agent de gonflement du gel, interfèrent avec le dégonflement de la viscose durant la régénération: citrate > thiosulfate > tartrate > sulfate > chlorure = phosphate = thiocyanate > acétate > nitrate > contrôle. L'iodure de sodium n'affecte pas le dégonflement ordinaire des films; le sulfure de sodium et le carbonate de sodium provoquent un dégonflement des films légèrement plus important que l'échantillon de controle. On propose que l'efficacité des sels suit une série de Hofmeister ou lyotropique.

## Zusammenfassung

Verschiedene chemische Additivs werden gewöhnlich bei der Viskose verwendet, um das Quellen der erzeugten Fasern und Filme zu vermindern. Es wurde gefunden, dass der Zusatz anorganischer Natriumsalze zu Additiv enthaltender Viskose die Wirkung der Additivs verändert. Die folgenden Salze, in Reihenfolge ihrer Gelquellungswerte angeführt, beeinflussen die Entquellung der Viskose während der Regeneration: Citrat > Thiosulfat > Tartrat > Sulfat > Chlorid = Phosphat = Thiocyanat > Acetat > Nitrat > Leerwert. Natriumjodid beeinflusst die normale Entquellung der Filme nicht; Natriumsulfid und Natriumkarbonat verursachen eine nur wenig stärkere Entquellung der Filme als bei der Kontrollprobe. Es wurde angenommen, dass die Wirksamkeit der Salze einer Hofmeister-oder lyotropen Reihe folgt.