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# Studies on Viscose Insolubles*

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The composition and physical solution state of the viscose are factors which influence greatly the industrial applications and the end-product quality in manufacturing films and fibers from cellulosic materials by the xanthation process. The subject has been of considerable interest to numerous workers over a great number of years. The number of articles found in the literature is quite large and no attempt will be made to give a summary of the huge amount of work which has been done in the past on different aspects of this very complex problem.

The present article describes briefly some of the efforts and results obtained in these laboratories on certain facets of the exploration of the insolubles in viscose solutions by various microscopic techniques. The emphasis has been placed on that part of the insolubles which probably originated from the starting material.

Ordinary light microscopes are of limited usefulness in work with viscose solutions because a large part of the insolubles have refractive indices which are very close to the refractive index of the viscose solution itself. There are two techniques which are often useful in the study of viscose gels and can be applied with an ordinary light microscope: Congo red staining technique and the technique of mixing a very dilute titanium dioxide dispersion into the viscose. Both methods increase the contrast for part of the materials in the viscose solution; however, both methods are likely to produce artifacts in the form of regenerated viscose skins and membranes and, therefore, have to be used with caution.

A phase microscope, on the other hand, is a very excellent tool for this problem. The small light absorption differences between the objects and the surrounding medium are converted into amplitude differences by the phase microscope and provide sufficient contrast to make the objects readily visible. The following description of the particles found in viscose solutions is, therefore, mainly based on observations obtained with the phase microscope.

The undissolved materials in the viscose solution can be subdivided into several broad groups.

*A. Fragments of swollen cellulose fibers.* A typical example of the swollen fiber pieces found frequently in viscose solutions is seen in Figure 1. Sizes of the fragments and degrees of swelling vary considerably, but the

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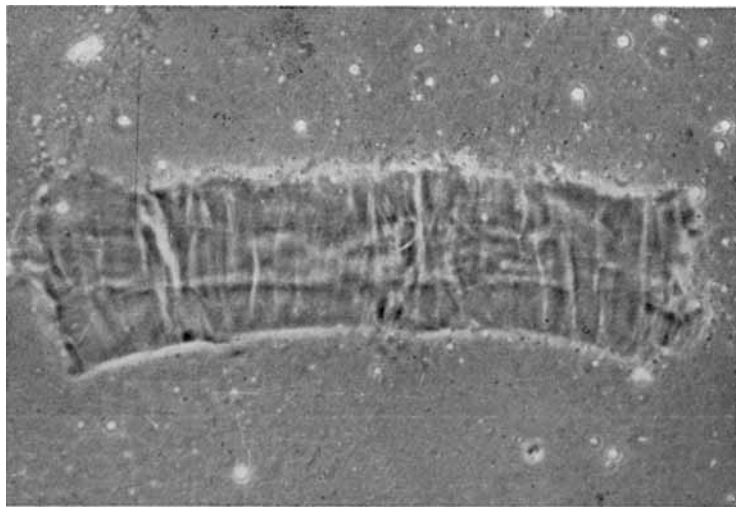

Fig. 1. A typical swollen fiber fragment in viscose solution as seen under the phase microscope. Particles surrounding the fragment belong to the group of the "granular dispersion." ×200.

general impression prevails that they are cut-out pieces from a whole fiber. These particles represent only a very small fraction of the total mass of the raw material. Under optimum viscose preparation conditions their numbers are considerably reduced and quite frequently these fragments can be completely eliminated. Although their fibrous nature is easily detected under the phase microscope, it is quite possible that these are the particles referred to frequently in the literature as the microscopic gel particles.

*B. Granular dispersions.* Particles in this group, usually in the size range of 1–5$\mu$, apparently are made up of very heterogeneous materials. The majority of these particles have an isodiametric shape, although slightly elongated particles are encountered rather frequently. Particles seen in the background of Figure 1 belong to this group. Due to the considerable depth of the viscose layer, a large portion of the particles is not seen in correct focus.

*C. Submicroscopic particles and possible superaggregates.* It is believed that a fraction of the undissolved material in viscose solutions is so finely dispersed that these particles cannot be detected with light microscopic techniques. Work in this area is in progress in our laboratories, and the results will be reported at some future time.

*D. Miscellaneous particles.* This group is very heterogeneous. Such materials as dust, field dirts, sand particles, pipe scale, dried viscose skins, and membranes are classified as belonging to this group. Silica particles originating as cell inclusions could possibly be added here as a subgroup of particles. This group will not be discussed in greater detail in this presentation.

## DISCUSSION

With some exceptions, there are generally several thousands of particles in 0.2 ml. of viscose, in the size range 4–50 $\mu$ as determined with the Coulter Counter.[1] Microscopic measurements usually substantiate these findings if due considerations are given to the differences in "size" as determined by each of these two methods. Correction factors are necessary if the two-dimensional parameters from microscopic measurements have to be correlated with the three-dimensional ones determined with the Coulter Counter.

In addition to the above differences in numbers of particles, the differences in types of particles appear to play an important role in the filtration process of the viscose solutions. Several experimental approaches were used in order to investigate and characterize the different kinds of the particles.

One-step chromium surface replicas were mainly used for the electron microscopy part of the investigations. The surface of a sulfite pine fiber fragment, as seen in Figure 2, appears rather smooth and structureless. Closer examination reveals a very finely grained texture. Several of the fiber pieces show a recognizable fibrillar network. The surface of the sulfate pine fiber fragments shows a much coarser and a more definite texture (Figure 3). Although individual cellulose fibrils are not discernible, it is quite possible that they are the cause of this texture. On comparison of these two types, the fragments of the sulfite fibers give the impression of being covered with a thin layer of viscose solution. It is possible to speculate that such a layer acts as a lubricant, allowing these particles to be squeezed through filter orifices.

The usefulness of a polarizing microscope in studies of cellulosic materials is based on their anisotropy. It is now generally agreed that the anisotropy is due to the alignment of the cellulose chains in the fibers. A cellulosic fiber with the chains aligned parallel to its axis behaves as a positive uniaxial medium with two refractive indices. Practical applications of these basic principles are, however, quite complicated. For example, the wall of a cellulose fiber contains different layers with differently oriented fibrils in each of the layers. Viewed simultaneously in the microscope the two opposite fiber walls display a great variety of cellulosic layers with different chain alignments in each of them. The resulting structure is known as the compound plate structure. Another complicating factor is the incompletely understood phenomenon known as the swelling birefringence: the birefringence values increase with increased swelling of the cellulosic fibers.

For our studies of the swollen fiber fragments in viscose solutions, the retardation of the electric vector by the particles was determined, with use of the Senarmont principle of compensation.[2] Figure 4 shows results obtained by plotting the phase difference in degrees ($y$-axis) against the fiber width (representing the degree of swelling) in microns ($x$-axis) of

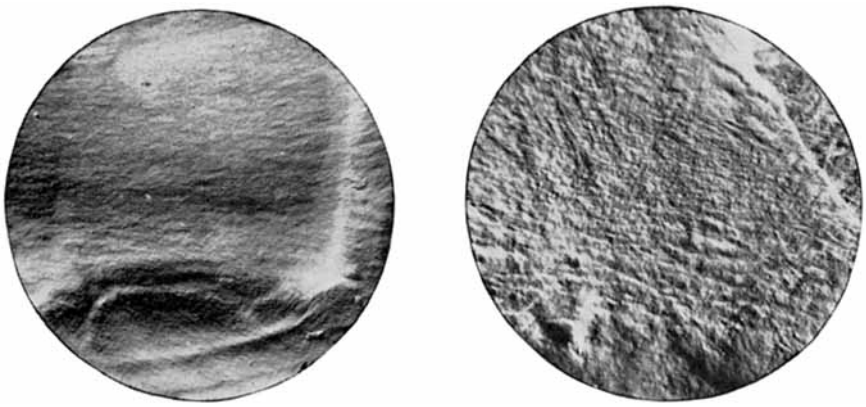

Fig. 2. Surface replica of a pine sulfite fiber fragment. ×5000.

Fig. 3. Surface replica of a pine sulfate fiber fragment. ×5000.

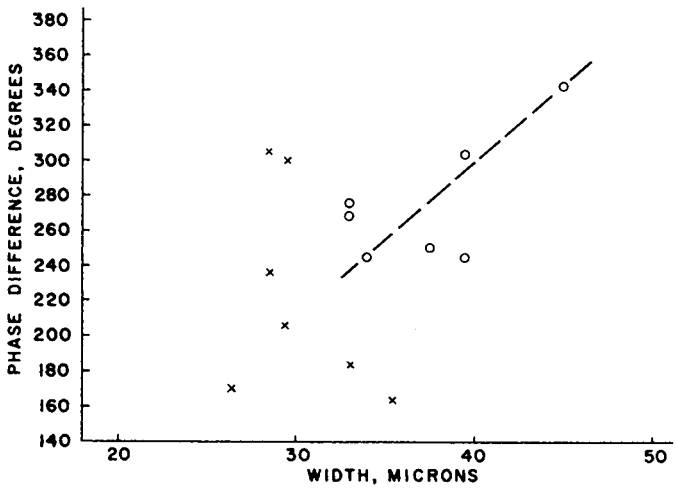


Fig. 4. Pine summerwood pulp fibers: (×) air dry; (O) swollen in 18.5% caustic.

native sulfate pine summerwood fibers. The air-dry fibers exhibit a considerable scatter with no apparent correlation between the two parameters. The fibers swollen in 18.5% caustic solution show a positive correlation believed to be due to swelling birefringence.

As seen in Figure 5, pine sulfite fiber fragments in viscose solutions are separated into two distinctly different distributions. The first distribution contains fragments which are smaller than 55 $\mu$ in width. These particles show a considerable scatter, with a low negative correlation between the birefringence and the degree of swelling. The fragments from the second distribution are wider than 55 $\mu$ and have a very high positive correlation. The fragments from sulfate pine fibers show an over-all higher degree of swelling. With few exceptions, the majority of these particles

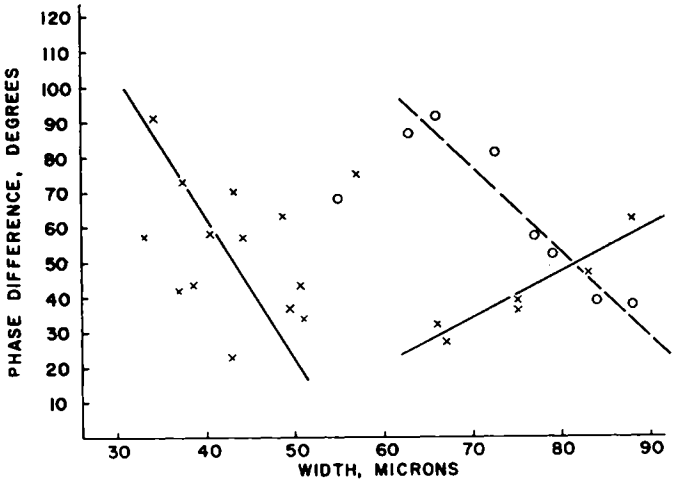


Fig. 5. Pine fiber fragments: (×) sulfite; (O) sulfate.

have a negative correlation between their birefringence and degree of swelling. Since the birefringence values of native fibers are considerably higher, a part of the fiber wall material is apparently dissolved. It is believed that the distribution of particles exhibiting the negative correlation represents particles consisting mainly of the more resistant fiber wall material which is not completely xanthated. The particles with the positive correlation, on the other hand, can be presumed to consist of alkali cellulose which has not been xanthated at all.

The $S_1$ layer covering the surfaces of almost all of the pulp fibers is more resistant, as a general rule, to the chemical reactions than is the rest of the fiber wall in viscose preparation processes. This layer restricts the swelling of pulp fibers considerably. The restricted swelling is believed to be often responsible for the fact that fragments of the fibers are incompletely xanthated, or are not xanthated at all. Incomplete access of the reagents to the bulk of the cellulose causes only a partial dissolution of the material and the fiber fragments involved remain undissolved in the final solution. The material in the $S_3$ layer is also much more resistant than the bulk of the material from the $S_2$ layer.

A considerable portion of the granular dispersion apparently represents finely dispersed materials from the more resistant parts of the fiber walls. Evidence obtained with the phase and polarizing microscope indicates that a part of the materials involved are carbohydrates and another part is lignin residues. The rest of the particles in this group comprise different inorganic materials with a rather diverse composition. Figure 6 shows a surface replica from a pine sulfate fiber fragment with impressions believed to have been left by particles of "granular dispersion type." Slightly larger particles of the same type are seen in Figure 7. The particles appear to be closely attached to the fiber fragment. Very rarely

Fig. 6. Impressions of small particles on the surface of a swollen pine sulfate fiber fragment. ×5000.

Fig. 7. Impressions of larger particles on the surface of a swollen pine sulfate fiber fragment. ×5000.

are such cases found on electron micrographs of surface replicas from pine sulfite fiber fragments. It appears that, even if the sulfite fragments seem to be penetrated with the solvent, the sulfate fragments are either closer to a true gel state or are closely associated with gel-like materials.

## SUMMARY

The microscopic investigations of insolubles in viscose solutions have shown that, generally, four groups of solid particles can be found in various amounts: (*1*) swollen fiber fragments, (*2*) granular dispersions, (*3*) submicroscopic particles, (*4*) miscellaneous particles.

All particles in the first and the third groups undoubtedly originate from the pulp starting material. It is believed that a considerable part of the material in the second group originates from the same source. However, particles from the fourth group are probably introduced for the most part as contaminants during the preparation of the viscose solutions. Only a small part of the fourth group, such as field dirts and silica cell inclusions, are traceable to pulp raw material.

A large portion of the insolubles in viscose must be removed or reduced in number by expensive filtration processes before casting or spinning satisfactory end products is feasible. Microscopic characterization of these viscose insolubles allows one to speculate about the source of origin and the mechanism involved in generating the various particles.

## References

1. Parks, L. R., and K. A. Jurbergs, *J. Appl. Polymer Sci.*, **4**, 193 (1960).

2. Hartshorne, N. H., and A. Stuart, *Crystals and the Polarizing Microscope*, 2nd ed., Edw. Arnold, London, 1952, p. 455.

## Synopsis

An investigation of the insolubles found in viscose solutions and various microscopic techniques are described. The emphasis is placed on substances which apparently originate from the pulp starting materials. Viscose insolubles may be subdivided into four broad groups: swollen fiber fragments, granular dispersion, submicroscopic particles, and miscellaneous particles. The electron microscope and polarizing microscope reveals characteristic differences between the swollen fiber fragments from sulfate pine pulps and those from the sulfite. Comparison with the original pulp fibers shows that these fragments contain primarily the more resistant parts of the fiber wall; the resistant layers are principally the $S_1$ and the $S_3$ layers and also a fraction of the $S_2$. Light and electron microscope studies indicate that the granular dispersions comprise different heterogeneous materials; fiber debris, lignin residues, and inorganic materials appear to be the main constituents in this group. Silica particles, originating as cell inclusions, and some dirt particles are the only miscellaneous materials traceable to the pulps; the others originate as contaminants from the viscose process and equipment.

## Résumé

Ce travail décrit les recherches effectuées sur les résidus insolubles des solutions de viscose et différentes techniques microscopiques sont décrites. On met l'accent sur les substances qui proviennent apparemment des matériaux pulpeux de départ. Les résidus insolubles de viscose peuvent être divisés en quatre grands groupes: les fragments de fibres gonflés, la dispersion granulaire, les particules submicroscopiques et les particules variées. La microscopie électronique revèle des différences caractéristiques entre les fragments de fibre gonflés provenant des pulpes de pin traitées au sulfate et au sulfite. De plus ces différences sont élucidées si on emploie le microscope polarisant. La comparaison de ces fragments avec les fibres provenant de la pulpe originale initiales montre que les fragments contiennent en principe les parties les plus résistantes de la paroi de la fibre. Les couches résistantes sont formées surtout des couches S et $S_3$ et également d'une fraction de $S_2$. Les études au microscope ordinaire et électronique indiquent que les dispersions granulaires contiennent différentes substances hétérogènes. Des débris de fibres, des résidus de lignine, et des substances inorganiques semblent être les principaux constituants de ce groupe. Des particules de silice, provenant des inclusions cellulaires, et quelques particules de poussières sont les seules substances parmi les différentes particules pouvant provenir des pulpes. Les autres particules proviennent de la contamination provenant de la technologie de la viscose et de l'équipement.

## Zusammenfassung

Eine Untersuchung der in Viscoselösungen aufgefundenen unlöslichen Bestandteile wird durchgeführt und verschiedene mikroskopische Methoden werden beschrieben. Das Hauptgewicht wird auf die Substanzen gelegt, die offenbar aus dem Ausgangsmaterial für den Pulp stammen. Die unlöslichen Bestandteile in Viskose können in vier grosse Gruppen unterteilt werden: Bruchstücke gequollener Fasern, eine körnige Dispersion, submikroskopische Teilchen und diverse andere Teilchen. Elektronenmikroskopische Aufnahmen zeigen charakteristische Unterschiede zwischen gequollenen Faserbruchstücken aus Sulfat- und Sulfitkieferpulp. Eine weitere Aufklärung dieser Unterschiede wurde durch Anwendung polarisationsmikroskopischer Methoden erhalten. Ein Vergleich dieser Bruchstücke mit den ursprünglichen Fasern zeigt, dass die Bruchstücke hauptsächlich die widerstandsfähigeren Bestandteile der Faserwand enthalten. Die widerstandsfähigen Schichten sind hauptsächlich die $S_1$- und $S_3$- und auch ein Teil der $S_2$-Schichten. Licht- und elektronenmikroskopische Untersuchungen zeigen, dass die körnigen Dispersionen aus verschiedenartigen, heterogenen Materialien bestehen. Fasertrümmer, Ligninrückstände und anorganische Stoffe scheinen die Haupt-

bestandteile dieser Gruppe zu sein. Kieselsäureteilchen, die von Zellinclusionen herrühren, und gewisse Schmutzteilchen sind unter den diversen anderen Teilchen die einzigen Substanzen, die aus dem Pulp stammen. Der Rest dieser Teilchen rührt als Verunreinigungen vom Viskoseprozess und den Apparaten her.

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