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Factors Influencing the Role of Additives During the Regeneration of Cellulose from Viscose Solutions

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INTRODUCTION

Success in producing super rayons can be attributed to a number of factors: developments in the handling and processing of viscose; modifications of the fine structure, e.g., effect of chain length, molecular weight distribution, size, shape, and amount of crystalline material; and the use of viscose additives or modifiers to control rates of coagulation and regeneration and to reduce primary swelling of gel fibers. In this paper some of the factors involved in the mechanism of viscose additives are discussed.

Viscose yarn can be improved by the reduction of the primary gel of the fibers. Additives which have been successful in reducing the degree of swelling include the following types, as indicated in patent literature: aliphatic amines,[1] dithiocarbamates,[2] some alkylene oxide compounds,[3] alkylene oxide derivatives of amines,[4] amides,[5] fatty acids,[6] and the like. Also the addition of zinc sulfate to the coagulating bath has been known for a long time to reduce the degree of swelling. Other metallic sulfates, such as ferrous, manganous, and chromic sulfates, have also been disclosed in this capacity.

Various researchers have studied the relationships of the degree of swelling to the concentration of the spin bath and the type of viscose, i.e., the degree of swelling in relation to the amount of sodium sulfate,[7] the degree of polymerization of the cellulose,[8] the concentration of the cellulose,[9] and the xanthate ratio of the viscose.[10]

The degree of swelling of the primary gel resulting from the coagulation of viscose in a concentrated salt solution is quite high. With a normal viscose containing 8% cellulose, the ratio of the volume occupied by 1 g. of cellulose in the gel and in the viscose is roughly 2 to 3.[11] Further, the degree of swelling is quite constant in the range of 12–17% sodium sulfate and is increased with more dilute solutions.[7] The effect of the composition of viscose on swelling has also been demonstrated. By holding the degree of polymerization constant, it has been found that the primary degree of swelling decreases as the cellulose concentration increases;[9] upon reversal of this procedure, the swelling decreases as the degree of polymerization increases.[8] The xanthate ratio apparently does not influence the degree of swelling.[10]

The experimental work described in this paper was limited to the study of the interactions of zinc, caustic, sulfur, and viscose additives. Two typical additives were investigated: (*1*) a polyoxyalkylene derivative of a fatty acid ester and (*2*) the primary amine, cyclohexylamine. A standard viscose was used and studies were made of the effects these additives have on the reduction of the degree of swelling of the cellulose gel and the retardation of the rate of neutralization of the alkaline gel by a typical viscose coagulating and regenerating bath.

The viscose used in this study does not necessarily make a super yarn. By minimizing factors such as the high degree of polymerization and favorable distribution of the crystalline regions, it was thought that the effects of the modifiers could be studied more conveniently. A "white" viscose[12] prepared by passing viscose over an anion exchange resin to remove sulfur-containing byproducts, was also used. The amount of sulfur in the form of by-product was then controlled by mixing "white" and regular viscoses.

EXPERIMENTAL

Viscose, prepared in the conventional manner using 8% cellulose and 6.5% sodium hydroxide, was ripened to a sodium chloride salt index of 11 (total sulfur, 2.45; xanthate sulfur, 1.54). This viscose (100 g.) was then slowly poured into a vigorously stirred solution of 0.3 g. Congo Red indicator in 20 g. of water at 25°C. After dilution of the viscose, 0.5 g. of the additive was added and the stirring was continued for an additional 0.5 hr. In these studies dealing with the effects of the sulfur by-product, the viscose was freed of its by-product, sodium trithiocarbonate, by passing it over a basic anion exchange resin, Amberlite XE-78. This resin treated viscose, the so-called "white" viscose, was then diluted in the manner described above and mixed with various amounts of conventional viscose for preparing a test sample with indicated concentrations of the by-product sulfur.

The viscoses were cast into films on a glass plate using a stainless steel film applicator which was 4.5 in. long, 0.5 in. diameter and was cut to a depth of 0.01 in. over 2 in. of its length. With Congo Red as the acid-base indicator, alkaline viscose was red and turned blue after being neutralized in the regenerating bath (a solution consisting of 7% sulfuric acid, 12.5% sodium sulfate, and 10.5% zinc sulfate). The films were held in the bath at 25 ± 1°C. for 60 sec. While in the spin bath, the film adhered to the glass plate and the acid-salt solution penetrated the film for the most part from the top only. This technique differs from a spinning operation in which the fibers are subjected to the spin bath solution from all directions.

A sample of the coagulated film was cut from the center portion, blotted with absorbent pulp sheets, and weighed. The weighed sample was washed free of bath acids and salts and dried 4 hr. at 105°C.

A gel swelling factor was calculated from the ratio of the gel weight (weight of the blotted but unwashed film) to the cellulose weight (weight of the washed and dried film). Some of the values reported refer to the gel swelling ratio which is the numerical value of the ratio of the gel swelling of the modified film to the gel swelling of the control.

In addition to the gel swelling measurements, the rate of neutralization of the viscose film was measured in the coagulating and regenerating bath. It is the number of seconds required for the Congo Red indicator in the viscose to change from red to blue. The numerical value is related to the so-called "D" value used in fiber studies, a measure in inches that the yarn travels before the indicator changes color. In general, the additives reduce the rate of neutralization, and the ratio of the rates of neutralization of the modified to the unmodified films is usually greater than one and is referred to in this study as the neutralization ratio.

The film technique was found to be reliable for measuring gel swellings and rates of neutralization. The volume changes usually attributed to the extension of filaments were absent in these studies. Orientation normally associated with a glass surface was negligible due to the relatively large thickness of the film. A minor amount of deformation resulted from the emission of gas bubbles, as well as the entrapment of gases during regeneration, and this error was inherent in the method.

Five determinations were made for each test sample, and the maximum deviation was ±5% for gel swellings and ±10% for neutralization rates. The rate of neutralization was taken as the total number of seconds that the viscose was in the spin bath before the acid-base indicator changed. The gel swellings were determined on the same films after having been kept in the spin bath for a total of 60 sec. In this 1-min. period, experiments showed that the gel swell factors had leveled off, and errors were thus minimized.

RESULTS AND DISCUSSION

The factors studied and found to affect the gel swelling and rates of neutralization of viscoses are (*1*) alkali, (*2*) viscose additives, (*3*) zinc sulfate, and

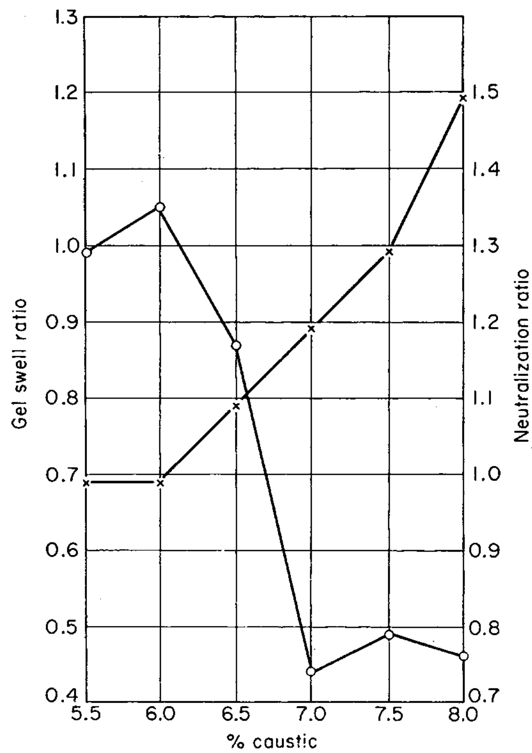


Fig. 1. (O) Relation of the caustic concentration and the gel swell ratio; (×) relation of caustic concentration and neutralization ratio.

(4) sulfur by-product. Some of the other variables which affect these factors such as the salt content of the spin bath, the type, concentration, and degree of polymerization of the cellulose, and the procedures for making the viscoses and the films were held constant.

1. Effect of Alkali

Experiments with six viscoses containing 6.5% cellulose and 5.5 to 8% alkali demonstrated that a marked decrease in the gel swell factors was found as the caustic concentration of the viscose was increased. The reduction in gel swell factors leveled off at about 7% (see Fig. 1). The retardation of the neutralization rate increased with increasing caustic concentration.

2. Effect of Additives

On immersing a film of the additive-containing viscose into the spin bath, the color change of the film was delayed to 14 sec. as compared with 7 sec. for the same viscose without additive (See Table I). Apparently the additive slowed the penetration of the acid into the film and the dye retained the red (basic) color for a period twice as long as with the control.

TABLE I
Coagulation and Regeneration Effects of Viscose Additives

Sample	Neutralization ratio	Gel swelling ratio
Control	1 (7[a])	1 (5.3[a])
0.5% Polyethylene oxide derivative[b]	2	0.57
0.5% Cyclohexylamine	1.8	0.55

[a] The numerical value which was measured.
[b] Based on viscose.

Along with the delayed neutralization, the additive-containing viscose had a lower gel swell factor. Although no effort was made in this work to compare the relative efficacies of various modifiers, it is probable that one can select a modifier on the basis of its relative ability to retard the neutralization and cause a lowering of gel swell. Table I contains data showing a delayed neutralization and a reduced gel swell factor which are caused by the additive.

3. Effect of Zinc Sulfate

a. Without Additive

Patent literature proposed the addition of zinc sulfate to the coagulating bath. The film technique demonstrated that the presence of zinc in the spin bath reduced the gel swell factor by a small amount in a bath of the same sodium sulfate concentration. However, on adjusting the salt content on the basis of specific gravity, the effect of zinc was not evident. The rate of neutralization, at least for films, was unchanged by the addition of zinc sulfate (Table II).

b. With Additive

The combination of zinc with the polyethylene oxide additive resulted in a twofold lowering of the gel swell ratio and a similar increase in the neutralization ratio. In the absence of zinc, both the rates of neutralization and the reduction of the gel swell factor remained essentially unchanged from the values obtained without an additive (Table II). From these data it is evident that the zinc ions must interact in some way before the additive becomes effective.

TABLE II
Effects of Zinc Sulfate

Spin bath composition (sulfuric acid–sodium sulfate–zinc sulfate)	Neutralization ratio	Gel swelling ratio
1. Without additive		
7–12–10.5	1	1
7–12–0	1	1.1
7–28.7–0[a]	1	0.95
2. With polyethylene oxide derivative		
7–12–10.5	2	0.5
7–12–0	1.1	1.1
7–28.7–0	1.1	1.0

[a] Sodium sulfate was adjusted so that the specific gravity of the salt solution was the same as the 7–12–10.5 spin bath.

4. Effect of Sulfur By-product

In the conversion of alkali cellulose to cellulose xanthate an unavoidable secondary reaction occurs in which sodium hydroxide and carbon disulfide react, for the most part, in the following manner:

$$3CS_2 + 6NaOH \longrightarrow NaCO_3 + 2Na_2CS_3 + 3H_2O$$

The sodium trithiocarbonate formed is referred to as by-product sulfur and corresponds, for practical purposes, to the carbon disulfide which is not bound as the xanthate. Sodium trithiocarbonate is responsible for the orange tint of viscose, and it can be removed by passing the viscose over a strongly basic anion exchange resin. In the preparation of this "white" viscose, it is important that the

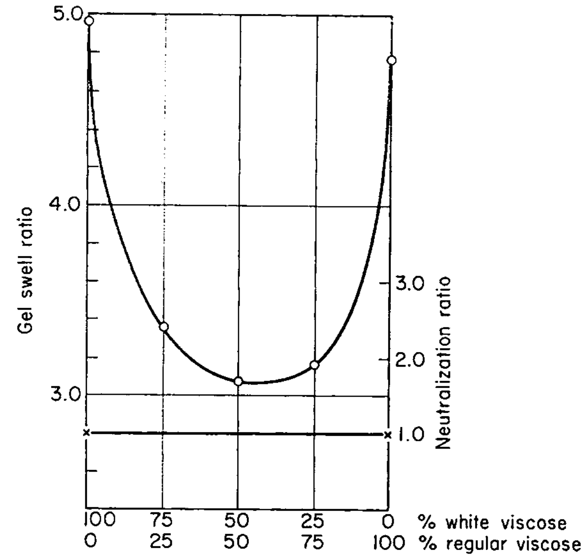


Fig. 2. Viscose without additive. (O) Relation of by-product sulfur with gel swell values; (X) relation by by-product sulfur with neutralization ratio.

hydroxide form of the resin be used in order to avoid the introduction of the chloride ion from the resin.

Viscoses with various amounts of sulfur by-product were prepared by mixing "white" with conventional viscose. As can be seen in Figure 2, in the absence of an additive, both "white" and regular viscoses had about the same numerical gel swell value, and a minimum value in gel swell occurred for the viscose consisting of an equal mixture of "white" and regular viscose.

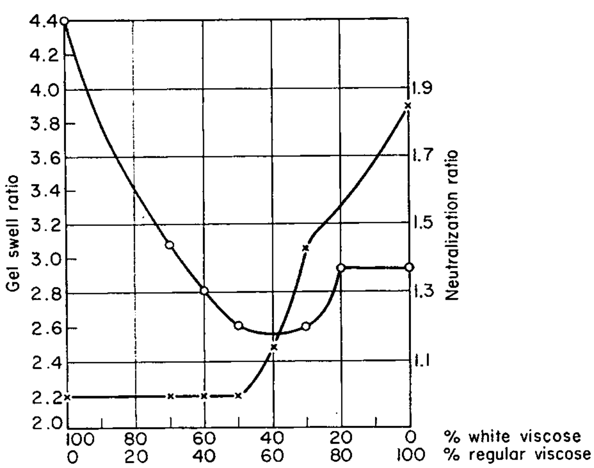


Fig. 3. Viscose containing 0.5% of a polyoxyalkylene derivative of a fatty acid ester. (O) Relation of by-product sulfur and gel swell ratio; (X) relation of by-product sulfur and neutralization ratio.

The rates of neutralization were unaffected by the presence of the sulfur by-product and this is shown in Figure 2 as a flat, straight line.

On the other hand, a different picture was obtained when a viscose containing an additive was used. Figures 3 and 4 show the results obtained by plotting gel swell factors of viscose versus per cent of by-product sulfur in the presence of the polyethylene oxide derivative and cyclohexylamine, respectively. The gel swell factors of the white viscoses with additives were approximately

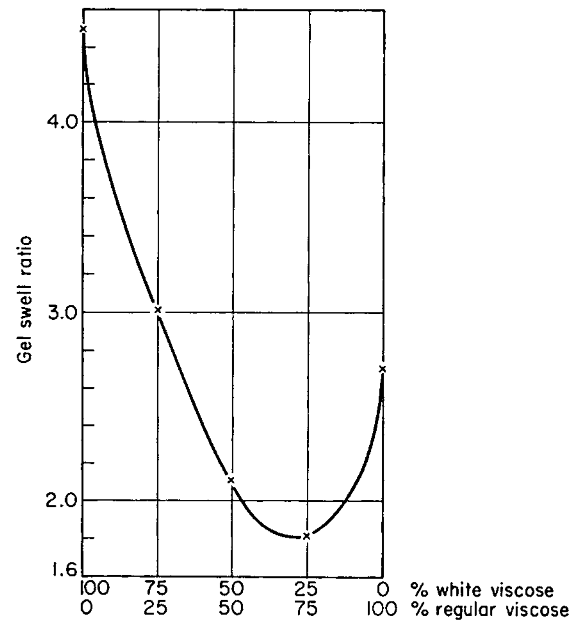


Fig. 4. Viscose containing 0.5% cyclohexylamine. (X) Relation of by-product sulfur and gel swell ratio.

the same for white viscoses without additives. As the by-product sulfur increased, the gel swell decreased and a minimum point was reached at 50–75% by-product sulfur in both modified and unmodified viscoses. The actual numerical values of the gel swells were considerably lower for the viscoses which contained additives as compared to those without an additive, and the value obtained for cyclohexylamine was lower at the minimum than the value for the polyethylene oxide derivative, as shown in Figures 2, 3, and 4. Whereas the viscose without an additive gave a symmetrical curve as the by-product sulfur was increased to 100%, the gel swell values of the viscoses with additives increased slightly and leveled off in the case of the polyethylene oxide additive.

A gradual retardation of the neutralization rate was observed as the amount of by-product was increased in viscoses containing polyethylene oxide, Figure 3.

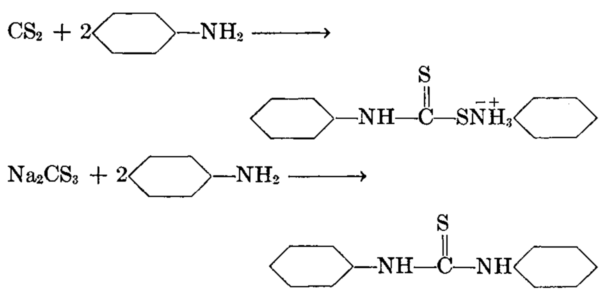
The experimental data indicated that all three materials, zinc ions in the spin bath, the additive, and the sulfur by-product in the viscose had to be present to obtain the desired effect—a reduction of the primary gel of the film. Thus, white viscose which contained an additive and was coagulated in a bath containing zinc had about the same gel swell and neutralization ratios as unmodified viscose, Figures 3 and 4. Similarly, no changes in swelling or neutralization were observed with a viscose which contained an additive but was coagulated and regenerated in a bath which contained no zinc (Table II).

In order to arrive at a mechanism that will explain the retardation of neutralization rates and the reduction of the gel swell ratio, it is important that the interaction of zinc ions, by-product sulfur, additive and cellulose xanthate be considered. Smith[13] considered some of the chemical mechanisms that have been suggested for the retardation of regeneration processes and concluded that none of the theories is completely satisfactory. Similarly, our work has not progressed sufficiently, nor is our present method of study adequate for proving a mechanism. However, we should like to speculate on this subject in view of some of our observations.

It has been observed that zinc cellulose xanthate is formed during the coagulation of viscose by an acidic zinc solution. Data obtained in our laboratory show that the zinc salt of cellulose xanthate can be formed almost quantitatively, i.e., one zinc ion for two xanthate units, in the absence of by-product sulfur at a pH level between 5 and 6. It has also been demonstrated that in the presence of by-product sulfur, the zinc also reacts with the sulfur by-products. However, these reactions do not explain the results of Table II and Figure 2, viz., almost identical gel swell ratios and neutralization ratios with or without zinc ion or by-product sulfur. Thus, it appears that the formation of zinc xanthate and zinc by-product sulfur compounds during a spinning cycle is only part of the chemistry involved.

In addition, it is important to note that although the polyethylene oxide is ordinarily considered inert, some of the cationic and nonionic polyethylene oxide compounds may form reaction products with a metal cation and an appropriate anion. This type of reaction which was discussed by Wurzschmitt[14] may occur during the coagulation and regeneration of cellulose from an additive-containing viscose. Thus, the quite insoluble polyethylene oxide derivative used in our experiments probably coagulates on coming into contact with the spinning solution; almost simultaneously the zinc ions react with sulfur by-products giving insoluble zinc-sulfur products which then coordinate with the zinc and the precipitated additive to form a semipermeable membrane between spin bath and the forming cellulose gel. It is possible that some cellulose xanthic acid could serve in this complex as a heteropoly acid, as described by Wurzschmitt,[14] to effect precipitation of the membrane which slows the diffusion of hydrogen ions but permits the coagulation of the gel.

In the case of an amine type additive such as cyclohexylamine, it is known that the amine can react with free carbon disulfide to form dithiocarbamates or with sodium trithiocarbonate to form thioureas:



The dithiocarbamate may form a zinc dithiocarbamate during the initial coagulation and this compound may then cause the modifying action in coordination with zinc and by-product sulfur reaction products. In practice it has been found that polyamines are more effective in retarding neutralization than monoamines and this may be explained by the more favorable conditions for precipitation of a crosslinked semipermeable membrane consisting of zinc cations, sulfur anions, and dithiocarbamates of polyamines. On the other hand, it has been found that very low molecular weight amines are not as effective as high molecular weight amines as viscose modifiers, because the low molecular weight amines are relatively soluble and may not readily form a semipermeable membrane.

SUMMARY

A mechanism has been proposed, based on data obtained from gel swelling and neutralization ratios, that involves the formation of a semipermeable membrane consisting of the viscose

additive, the by-product sulfur, and zinc ions. The full extent of the additive is apparent only when the above-named components are present in the viscose and the spin bath.

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Synopsis

The influences of caustic, zinc, by-product sulfur, and additives on the degree of swelling and the rate of neutralization of viscose are reported. A film technique showed a marked decrease in gel swell factors as the caustic concentration was increased from 5.5 to 7%. In the presence of zinc and by-product sulfur, the viscose additive retards the regeneration process and reduces the gel swell. On mixing various amounts of "white" and conventional viscoses, a minimum value in gel swell occurs with an equal mixture of "white" and regular viscoses. A similar relationship is obtained on adding a polyethylene oxide derivative or an amine to the viscose; namely, a minimum point is reached at 50–70% by-product sulfur, but in these cases as the by-product sulfur is increased to 100%, the gel swell values level off. The actual numerical values of the gel swells are considerably lower for the mixed viscoses which contain additives in comparison with those without an additive. A gradual retardation of the neutralization rate is observed as the amount of by-product sulfur is increased in viscoses containing a polyethylene oxide derivative. A mechanism explaining the retardation of neutralization rates and reduction of the gel swell is proposed, based on the formation of a coordination complex between the additive, zinc ions, by-product sulfur, and the xanthate.

Résumé

On rapporte l'influence d'alcali caustique, de zinc, de soufre produit secondaire et d'additifs sur le degré de gonflement et la vitesse de neutralisation de la viscose. Une technique utilisant un film montre une décroissance marquée dans les facteurs de gonflement du gel quand la concentration en alcali caustique augemente de 5,5 à 7%. En présence de zinc et de soufre produit secondaire les additifs de la viscose retardent les processus de régénération et réduction du gonflement du gel. Si l'on mélange des quantités variables de viscose blanche et de viscose conventionnelle il se produit une valeur minima du gonflement du gel pour des mélanges égaux des deux viscose. On obtient une relation similaire si l'on ajoute un dérivé de l'oxyde de polyéthylene ou une amine à la viscose. Notamment on obtient un point minimum à 50–70% de soufre mais dans ces cas à mesure que la concentration en soufre tend vers 100% les valeurs de gonflement du gel tendent vers une limite maximum. Les valeurs numériques actuelles de gonflement du gel sont considérablement plus basses pour les mélanges de viscose contenant des additifs comparés à ceux sans additifs. Dans les viscoses contenant un dérivé de l'oxyde de polyethylene on observe un retardement graduel de la vitesse de neutralisation à mesure que la concentration en soufre augmente. On propose un méchanisme expliquant le retardement de la vitesse de neutralisation et la réduction du gonflement du gel sur la base de la formation d'un complexe de coordination entre l'additif, les ions zinc, le soufre secondaire et le xanthate.

Zusammenfassung

Es wird über den Einfuss von Alkali, von Zink, von abgeschiedenem Schwefel und von Additives auf den Quellungsgrad und die Neutralisationsgeschwindigkeit von Viskose berichtet. Eine Filmmethode liess eine merkliche Abnahme des Gelquellungsfaktors bei Erhöhung der Konzentration des Alkalis von 5,5 auf 7% erkennen. In Gagenwart von Zink und abgescheidenem Schwefel verzögert das Viskoseadditiv den Regenerierungsporzess und setzt die Gelquellung herab. Beim Vermischen verschiedener Mengen von "weisser" und üblicher Viskose, tritt bei Mischung gleicher Teile "weisser" und regulärer Viskose ein Minimum in der Gelquellung auf. Eine ähnliche Abhängigkeit wird bei Zusatz eines Polyäthlenoxydderivates oder eines Amins zur Viskose erhalten; es wird nämlich bei 50–70% abgeschiedenem Schwefel ein Minimum erreicht, jedoch tritt in diesem Fall bei Erhöhung des abgeschiedenen Schwefels auf 100% ein Ausgleich des Wertes der Gelquellung auf. Die tatsächlichen numerischen Werte für die Gelquellung sind für die gemischten Viskosen, die Additive enthalten, beträchtlich niedriger als für solche ohne Additive. Eine schrittweise Verzögerung der Neutralisationsgeschwindigkeit wird bei Viskosen, die Polyäthylenoxydderivate enthalten, mit steigender Menge des abgeschiedenen Schwefels beobachtet. Es wird ein Mechanismus zur Eeklärung der Verzögerung der Neutralisationsgeschwindigkeit und Herabsetzung der Gelquellung vorgeschlagen, dem die Bildung eines Koordinationkkomplexes zwischen dem Additive, den Zinkionen, dem abgeschiedenen Schwefel und dem Xanthat zur Grunde liegt.

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