

A STUDY OF COPPER-SODIUM HYDROXIDE-TARTARATE-CELLULOSE COMPLEX SYSTEM

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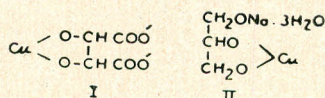
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Copper in an alkaline medium possesses the property of forming complexes with polyhydroxy compounds. The study of these compounds has been extended to cellulose and it has been observed that copper in a system like copper-sodium hydroxide-tartarate/glycerol, possess a preferential affinity for cellulose.

Copper in the copper-cellulose complex is believed to exist in an ionic form as it undergoes reactions with other anionic groups and can be successfully brought back into solution when this complex is placed in a blank solution containing tartarate and alkali only.

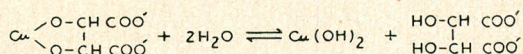
This reaction has been utilized to make cellulose resistant to bacterial degradation and the breaking load of cellulose before and after exposure to active soil has been compared, when cellulose treated as above and also with copper naphthate to give an equivalent amount of copper was tested under similar conditions.

Alkaline solution of copper in the presence of sodium potassium tartarate (Fehling's solution) is a common reagent and frequently used for the detection and quantitative estimation of reducing groups, such as aldehydic, in organic compounds. Copper in this complex form is kept masked, and constitutes a potential source where very mild and specific oxidation conditions are required. Until lately conflicting views were held regarding the manner in which copper exists in this solution and the two views being discussed presently have generally been accepted with respect to the existence of copper in Fehling's solution,¹ viz., that copper replaces the hydrogen atoms of the two hydroxy groups in the tartarate molecule as shown in (I).



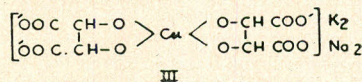
In a similar manner the mode of combination of copper with glycerol in the presence of free alkali is represented by (II). Whenever a reducing compound is brought in contact with these solutions, copper is readily available as $\text{Cu}(\text{OH})_2$ and further amounts are transferred from the states represented by (I) and (II) until either an equilibrium is attained, or no more of copper can react. It is possible to exhaust all the copper in this manner provided the end products are removed and fresh polyhydroxy compound is introduced in the solution.

Compound (I) has actually been isolated and it is immediately apparent that it is not a complex, but a primary valence compound and it has been argued that the precipitation of cupric hydroxide on heating a solution of (I) is based on the reversible hydrolysis:

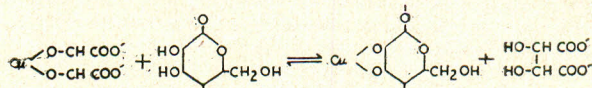


But Fehling's solution always contains an excess of tartarate and thus prevents the precipitation of cupric hydroxide through the mass action effect.

The second view explains the masking of copper in terms of a complex compound (III). The two views in this controversy have been merged together and it is believed that a Fehling's solution contains varying amounts of (I) and (III), and that they are active there.



Cellulose, like tartaric acid and glycerol, is a polyhydroxy compound and should therefore be expected to yield a similar complex with copper in the presence of free alkali. But the heterogeneity of the system (there being two solid components i.e., cupric hydroxide and cellulose) does not permit the formation of a complex. However, when cellulose is brought in contact with Fehling's solution in which copper is active but temporarily masked, the copper-cellulose complex is produced. This may be considered as a replacement reaction.



An equilibrium is readily established until cellulose can no longer react with copper. Copper becomes firmly attached to cellulose and may be removed by carrying out the reverse reaction, i.e., by putting the copper-cellulose complex in a solu-

tion of alkali and tartarate. The desorbing effect, too, reaches an equilibrium and for the complete removal of copper fresh portions of alkali-tartarate solution are required. The principle underlying the mechanism of these reactions has also been utilised for dissolving cellulose completely in the Fe^{+++} , NaOH-tartarate-cellulose system² by using very high concentrations of Fe^{+++} , NaOH and sodium potassium tartarate. A preliminary study of the iron-alkali-tartarate-cellulose system during the course of the present investigations has shown that in low concentrations iron reacts in the divalent form, imparting a greenish colour to cellulose, which on removal and washing in water, gets oxidised to the trivalent form giving a brown colour to cellulose. This is being studied in greater detail. The reaction of metals in alkaline medium with soluble saccharides in the absence of tartarate ion has also opened up another field for making medicinal preparations containing these metals.³⁻⁶

Normal concentrations of chemicals required for Fehling's solution were modified and adjusted so as to put desired amounts of copper on cellulose under different conditions of experiments. The maximum time allowed for an experiment did not exceed 30 minutes, although it was observed that a treatment lasting for 15 minutes only yielded amounts of reacted copper which were near enough the equilibrium values. Occasional agitation was considered adequate, while cellulose was kept submerged in the solution, and no particular care was taken to avoid chance contact with air during stirring or when cellulose was removed at the end of the experiment and rinsed well in running water. The resultant copper-cellulose complex was coloured greenish-blue, and the intensity of the colour varied with the concentration of chemicals used in the solution. This complex was found to possess a fairly high resistance to leaching by water and dilute solution of ammonia and also to the attack by bacteria when cellulose so treated was exposed to active soil by the conventional soil burial technique.

Experimental

Material and Reagents

Cotton fabric: Commercially bleached dosooti with the following details was used in these experiments: Weight per square yard, 7 oz.; ends and picks, 34/34 (both double); count: warp/weft, 14/14^s (42.2 Tex); breaking load, 6" × 7" for warp only (average), 418 lb. Pieces were cut and frayed to weigh between 9.9 and 10.1 g, except when the breaking load was to be determined,

in which case the size of the strips was 6" × 12". No further purification of the fabric was considered necessary.

All the chemicals were pure or A.R. type.

Stock solution containing 20 g. of copper per litre was prepared by dissolving the metal in nitric acid, expelling the acid and then neutralising the residual acid with small amounts of sodium carbonate.

The alkaline solution of tartarate contained 15.4% of sodium hydroxide and 35.2% of sodium potassium tartarate (Rochelle salt), both on weight by volume basis.

Except, when stated on the contrary, the ratio between the weight of the fabric and the volume of the solution used was kept at 1:10.

The experiments were conducted in 400-ml. beakers. The solution was brought to the desired temperature and the fabric introduced with gentle stirring. Precise control of temperature was maintained, except at 60°C. where the temperature was within $\pm 1^\circ\text{C}$. At the end of the experiment, the fabric was taken out, rinsed thoroughly in running water so that all traces of chemicals were removed and the amount of copper determined on oven-dry weight of the pieces. Strips required for the determination of breaking load or resistance to bacterial degradation were dried at room temperature and conditioned for breaking load or exposed to active soil.

Effect of Certain Variables on the Amount of Copper Reacting with Cellulose

(a) *Time*.—The effect of time on the reaction was studied by treating the pieces of fabric in a solution containing 0.20% Cu, 1.54% NaOH and 3.52%

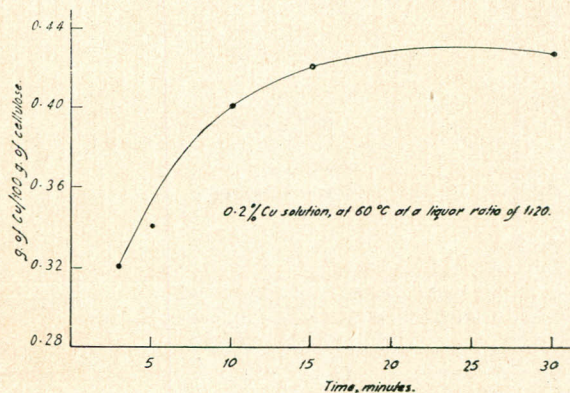


Fig. 1.—The effect of time on the amount of copper reacted.

of Rochelle salt at 60°C., the ratio of the volume of the solution of the weight of the fabric being 20:1. It can be seen from Fig. 1 that the equilibrium values are obtainable over short periods, giving indication of the reaction being of ionic nature and that prolonging the reaction will not serve any useful purpose.

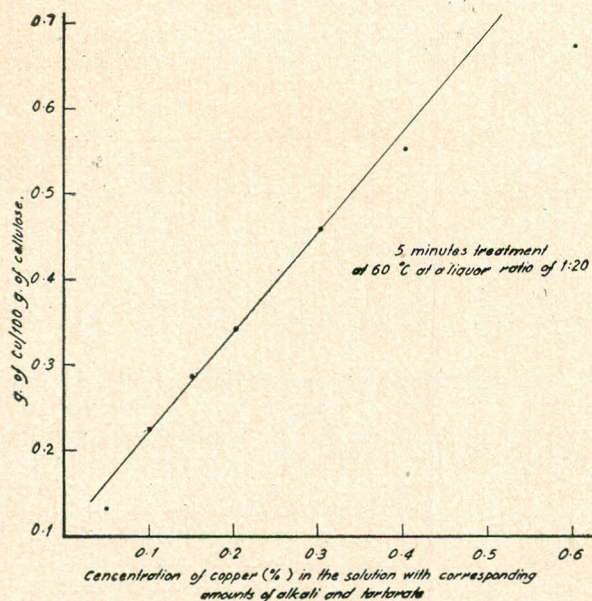


Fig. 2.—Showing the effect of the concentration of copper on the amount of copper reacted.

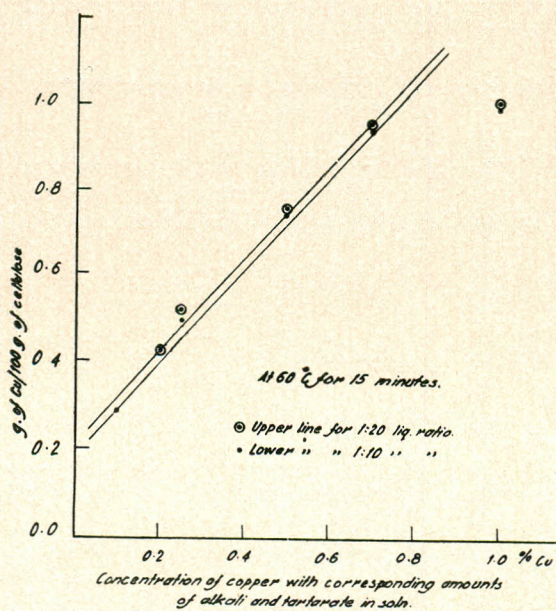


Fig. 3.—Showing the effect of volume of the copper soln. on the amount of copper reacted.

(b) *Concentration of Copper.*—Figure 2 predicts the effect of the concentration of copper when the reaction was carried out for five minutes at 60°C. and the volume of the solution used was 20 times the weight of the fabric treated. Fig. 3 shows the same effect when the reaction was allowed to proceed for 15 minutes employing liquor ratios of 10:1 and 20:1. In all these experiments, the proportion of chemicals, i.e., copper, alkali and tartarate was varied in accordance with the ratio of chemicals as in (a). For all practical purposes, the effect of the volume of the solution, at a fixed concentration of chemicals, on the amount of copper reacting with cellulose is almost negligible and the slope of the linear relationship is not affected in any way.

(c) *Effect of Temperature.*—For equilibrium or near-equilibrium times, the effect of temperature is shown in Fig. 4. The composition of the solution is the same as in (a) above and the liquor ratio 20:1. It can be seen that the rate of reaction of copper with cellulose increases with the rise of temperature and approximately between 45° and 55°C. the relationship is of a linear nature and below and above these temperatures it takes the form of a curve. Further at higher temperatures, i.e. at 60° and 70°C., the increase in the amount of copper reacted is not so pronounced and therefore all further experiments were conducted at 60°C.

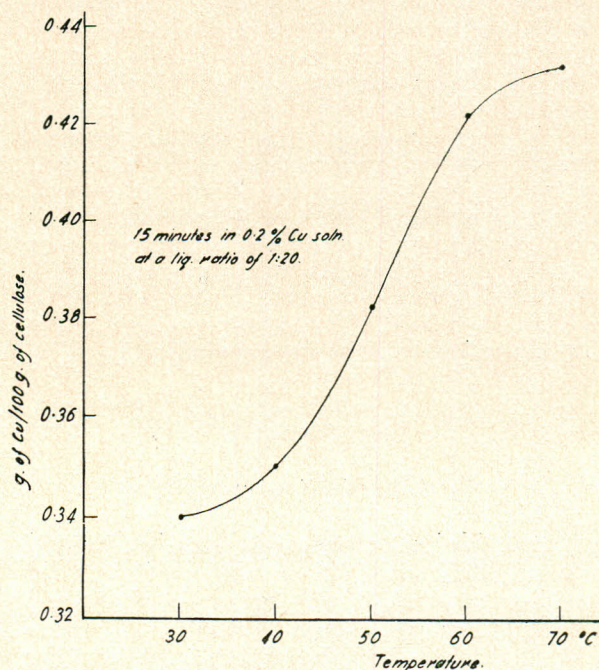


Fig. 4.—Showing the effect of temperature on the amount of copper reacted.

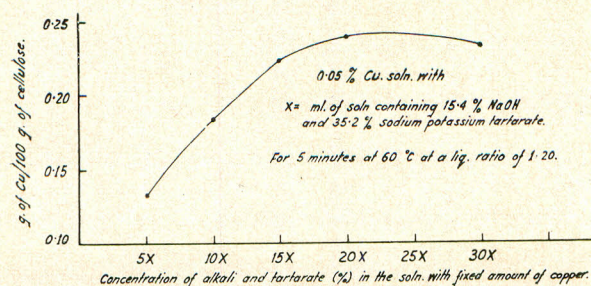


Fig. 5.—Showing the effect of alkali and tartarate on the amount of copper reacted.

(d) *Effect of Alkali and Tartarate.*—In this case the concentration of copper in the solution was always kept at 0.05%. The volume of the solution was 20 times the weight of the fabric and the experiments were conducted at 60°C. Figure 5 shows this effect. The amount of copper reacting with cellulose reaches a peak and then further increase in the concentration of alkali and tartarate produces a desorbing effect.

Resistance to Leaching by Water and Dilute Solution of Ammonia

(i) *Water.*—A piece of fabric treated to contain 0.65% copper on the oven dry weight was subjected to leaching action by putting it in running tap water for 24 hours. The rate of flow of water was approximately 400 ml. per minute. The residual amount of copper on the dry weight basis is given as follows: control, 0.65% Cu; residual, 0.51% Cu. (Cu retained, 78.4%).

(ii) *Ammonia.*—The treated fabric was put in a solution containing 1 g. of ammonia per litre at a

temperature of 34°C., the volume of the solution being 50 times the air dry weight of the piece. The solution and the fabric were placed in a conical flask and stoppered. The flask was occasionally shaken and the leaching action carried out for one hour. The results are: control, 0.75% Cu; residual, 0.56% Cu; (Cu retained, 74.6%).

Resistance to the Bacterial Degradation

Pieces were cut and frayed to measure 6" × 12" in size. Only warp threads were used for this purpose to minimise the chances of variations in the breaking loads. An appropriate number of such strips were weighed and treated to give a desired amount of copper.

Similarly another set of test pieces was prepared along the warp direction and padded in a solution of copper naphthenate in white spirit so that the final copper content on the dry weight basis was of the same order as above. It was rather difficult to get the two figures for copper content coincident with each other, but a fairly good agreement was found as will be seen from the data given below.

The air-dried pieces from both the sets were exposed to the soil for a period of 14 days under similar conditions. The soil used in these experiments was active enough to destroy completely the untreated control pieces of the fabric in 4 to 5 days, when simultaneously exposed to soil. After fourteen days, the strips were taken out, washed to remove soil, conditioned and their breaking loads determined. A comparative statement of the figures for copper content, breaking loads of the two sets before and after exposure for 14 days is given in Table I.

TABLE I.—COMPARATIVE STATEMENT OF COPPER CONTENT AND BREAKING LOAD.*

S. No.	Present work				With copper naphthenate			
	Cu %	Breaking load before exposure	Breaking load after exposure	strength retained%	Cu %	Breaking load before exposure	Breaking load after exposure	strength retained%
1.	0.29	417	81	19.4	0.31	450	80	17.7
2.	0.66	416	292	70.2	0.35			
3.	0.68	416	300	72.1	0.70	475	382	80.4
4.	"	"	291	70.0	0.70	487	444	90.1
5.	"	"	361	86.7	0.69	488	411	84.2
6.	"	"	258	61.5	"	"	402	82.4
					"	"	254	54.0

* Breaking load of the untreated fabric was 418 lb.

It will be seen from the above that copper naphthenate treatment increases the breaking load of dosooti by 7.4% when the percentage of Cu was at 0.31/0.35 and again by 13.4% when the percentage of Cu was at 0.69 to 0.70. On the other hand there was no corresponding increase in the values of the breaking loads whether copper-cellulose complex had lower or higher percentage of copper in it. In fact, no change in the breaking load was observed in this case even when the copper content stood at 1.0%

Since it was very difficult to interpret and correlate the breaking loads of pieces padded with copper naphthenate before and after the soil exposure due to the enhanced values of the breaking loads, the values of breaking load before exposure were made the basis for calculating the percentage, of strength retained in this case.

Reactivity with Other Chemicals

Reactivity of copper in the Fehling's solution is temporarily masked and copper is not precipitated out when additions of sodium carbonate, soap and sodium abeitate (abeitic acid dissolved in sodium hydroxide) are made to it. Further, these chemicals do not interfere with the reactivity of copper with cellulose. On the other hand, it has been found that copper in addition to undergoing a reaction with cellulose, simultaneously reacts with these chemicals and the resultant copper-cellulose complex carries the carbonate with it or a residue of fatty or abeitic acid. The latter two, particularly the copper soap produced *in situ* gives water-repellent characteristics to the fabric so treated, and it is therefore possible to deposit copper soaps on cellulose in one operation. Addition of sodium sulphide to Fehling's solution of such composition as used in these experiments instantaneously precipitates copper both in the solution as well as on the copper-cellulose complex.

Advantages of the Treatment

(1) The process is simple to carry out, and there are no complications involved.

(2) It ensures a uniform treatment.

(3) No special equipment or apparatus is required to carry out the process.

(4) Non-aqueous solvents are not required and therefore there are no fire hazards, toxic effects or chances of unpleasant odour.

(5) The treated cloth remains soft and does not have any adverse effect when in contact with human body.

(6) The materials are easily available and their application is economical. It has been found out that when one batch has been finished, another can be treated in the standing liquor by replenishing it with small amounts of chemicals. Three pieces, for example, treated successively in the same solution without replenishing it, gave the following copper contents: 1st, 0.65%; 2nd, 0.57%; and 3rd, 0.51%.

The fall in the copper content is not very sharp and by making good the loss of chemicals in the bath, cellulose can be treated almost to the same copper content.

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References

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