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IMPROVEMENT OF HEAT STABILITY OF PAPER MADE FROM SULFITE AND KRAFT PULPS

April 9, 1966

Robert Perry Lynn

## ABSTRACT

Paper made from bleached sulphite and sulphate pulps and then treated with sodium alginate and antimony resin solutions show far less physical and chemical degradation with heat than these same papers when not treated with these solutions. Sodium alginate and antimony resins solutions appear to inhibit degradation up to 175 C for 45 minutes but are not effective when the papers are heated to 210 C. for 45 minutes. The paper made with bleached sulphate pulp and saturated with sodium alginate solution showed an appreciable increase in folding strength when heated at 175C for 45 minutes, which is most unusual.

The presence of iron which might come from process water appears to negate the effect of alginate and antimony solutions and should be held to a minimum when making paper meant for unusual heat resistance.

Aquapel-kymene 557 sizing solution either inhibits chemical degradation as measured by the copper number test or else interferes with the test by blocking the reducing groups which are generally regarded as products of degradation. Upon heating the Aquapel-kymene 557 complex must break down and aid in degradation of the sample as shown by the copper number.

The permanence of paper might be enhanced if treated by the methods prescribed in this report. The utility of papers used for winding electric wires, for paper plates and for use on Virkotype presses might be improved with these treatments.

## SCORCH RESISTANT PAPER

The degradation which occurs when cellulose is subjected to high temperatures, i.e., over 100° C., is a source of concern for both paper and textile industries. In most practical applications, heat degradation shows up as a loss of strength and, as a result, most of the studies which have been made on the subject have been concerned primarily with strength considerations. However, any effort to improve the thermal stability of cellulose through chemical modification of the molecule requires a more fundamental understanding of the degradation reactions.

Many investigators have shown that the conditions under which cellulose is heated have a major influence upon the nature and extent of degradation. Waller, Bass, and Roseveare (1), in a study of tire yarn degradation at temperatures of 150 to 175° C., found that the strength loss was proportional to both the temperature and the amount of moisture present, and that the oxygen consumption was a function of the amount of moisture present. These authors suggested that the degradation under the conditions employed was a result of the formation and subsequent decomposition of oxidized cellulose. Farquhar, Pesant, and McLaren (2) heated raw unextracted cotton in air and nitrogen at temperatures of 75 to 220° C. for reaction times of 4 and 24 hr. It was found that carboxyl content, hydroxyl content, fluidity, weight loss, and resistance to enzymatic hydrolysis increased with temperature and time of heating; for any given temperature and time, degradation was greater in air than in nitrogen. It was concluded that "heat alone accounted for only a part of the degradation of cellulose," and that "oxidative action began at lower temperatures and accelerated thermal decomposition at higher temperatures."

The thermal stability of manila insulating papers was studied extensively by Clark (3). The influence of both air and moisture on degradation was investigated, and moisture was found to have the greater influence. In view of the loss of tensile strength which occurred when insulation was heated in an inert atmosphere, and marked influence of moisture, Clark suggested that "the fundamental change responsible for the deterioration of cellulose insulation in electrical apparatus involves the formation of hydrocellulose," although the formation of oxidized cellulose was also found to result in some loss of tensile strength, presumably due to thermal instability of the oxidized cellulose. The relative importance of oxidation and hydrolysis was felt to depend upon the conditions of heating, but pyrolysis was thought to be the most important degradation mechanism during prolonged heating. Honold, Poynt, and Cucullu (4) confirmed a portion of Clark's work by showing that the strength loss was greater when cotton fabrics were heated in water vapor at 160° C., than when the fabrics were heated in air at the same temperature. However, Conrad, Tripp, and Mares (5) concluded that the degradation of cotton yarn was oxidative rather than hydrolytic during heating at 110 to 150° C. in air at 40% R.H.

The importance of the temperature of degradation was stressed by Agster (6). Working with viscose rayon, he concluded that the primary degradation reaction was hydrolysis below 140° C., air oxidation between 140 and 160° C., and destructive distillation, or "cracking," above 160° C. Haas (7) also postulated a change in reaction with a change in temperature, suggesting that the degradation of cotton is primarily oxidative above 200° C., and primarily hydrolytic below 180°C.

Demus (8) measured the change in viscosity with time when cotton was heated at 150° C.; the decrease in viscosity became slightly less rapid after 50 hr. The presence or absence of oxygen had almost no effect upon

the decrease in viscosity when viscose rayon was heated at 150°C. However, Staudinger and Jurisch (9) found that the decrease in degree of polymerization was greater when cotton was heated in air than when it was heated in high vacuum. It was found that the D.P. drop after heating in air at 150° was the same whether the cotton was heated 2,4, or 6 days. No attempt was made to explain this effect and the complete reaction conditions were not given.

Cellulose is known to evolve certain gases, such as carbon monoxide, carbon dioxide, and water, during heating. The rate of evolution and the composition of the gas have been studied by Clark (3) and Murphy (10). Clark found that the manila insulating paper went through a "dormant period" upon heating, during which no gases were evolved. The composition of the evolved gas was found to be a function of the temperature of heating. Murphy found no evidence of the "dormant period" and determined that exposure to oxygen temporarily increased the amount of gas subsequently evolved under vacuum. Perlin (11) studied the heating of cellulose in which some of the primary hydroxyl groups had been oxidized, and found that the initial reactions at 255° were dehydration and decarboxylation. The evolved carbon dioxide was considered to come almost entirely from the uronic acid groups in the cellulose. In his book on pyrolysis (12), Hurd gives many illustrations of thermal decarboxylation, as well as the formation of carbon monoxide through thermal decarbonylation.

William D. Major (13) concluded that degradation in a dry oxygen atmosphere at 170°C. is a result primarily of oxidation, with oxygen acting as a nonspecific oxidant. These reactions take place primarily in the amorphous regions of the cellulose, and continue to occur after the degree of polymerization becomes constant.

H. A. Buchanan (14) determined the ignition temperature of Kraft and sulfite pulp to be about 260° C. In his article he explains that below such temperatures the material may suffer loss of weight and extensive decomposition as the ignition temperature is approached. At the ignition temperature the exothermic reactions increase and combustion will occur if enough oxygen is present.

The uncertainty which surrounds the heat degradation of cellulose is due probably to the marked influence which the conditions of reaction have upon the nature of the degradation. Oxidation, hydrolysis, and pyrolysis, or a combination of these, have been suggested as reaction mechanisms for the degradation by various authors.

Recently, National Starch (15) has produced a new antimony resin fire retardant, VI-Tard, which is expected to improve strength and optical properties of paper when subjected to high temperatures. It is hoped that by combining this resin with asbestos fiber a scorch resistant paper with good optical strength properties can be produced.

## EXPERIMENTAL PROCEDURE

### Kraft (K-Series)

The kraft pulp (Celgar Bleached Kraft) was beaten for one hour and made into handsheets using the Nobel and Wood Sheet Mold. There were two sets of samples made; one using deionized water in the mixing tank and the other without.

#### 1. Sheet Treatment

The samples were made up as follows: (K-1) 15 gm O.D. pulp; (K-2) 15 gm O.D. pulp; 6 gm Ketene dimer (Aquapel followed by Kymene); (K-3) 15 gm. O.D. pulp, .6 gm Ketene dimer and .5% solution of sodium alginate (Kelgin M.V.); and (K-4) 15 gm O.D. pulp, .6 gm Ketene dimer, and 1% sodium alginate. The average weight of the handsheets was 2.5 gm O.D. The sodium alginate solution was applied by a size press application.

### Sulfite (S-series)

The sulfite pulp (Puget Bleached Sulfite) was beaten for one hour and then made into handsheets using the Nobel and Wood Sheet Mold. There were two series S samples made. One was made using deionized water in the mixing tank and the other was made using ordinary tap water.

#### 1. Sheet Treatment

The sulfite pulp was made into handsheets and treated as follows: (S-1) 15 gm. O.D. sulfite pulp; (S-2) 15 gm O.D. sulfite pulp and 1.5 gm asbestos fiber; (S-3) 15 gm O.D. sulfite pulp, 1.5 gm asbestos fiber, and .78 gm. antimony resin (National Starch's VI-Tard); and (S-4) 15 gm O.D. sulfite pulp, 1.5 gm asbestos fibers, and 1.5 gm. antimony resin. The asbestos and antimony resin are wet end additions, and can be added at the beater or added at the machine chest.



## Testing Procedures

The samples were tested before heating and after heating for folding endurance and brightness. Fold was carried out by ASTM D-654-43 and brightness, according to ASTM D-985-50. The K series was also tested for copper number by ASTM D-919-49 in an effort to explain the unusual strength increase after heating.

## Heating

### 1. K Series

The first series consisting of regular tap water was heated to 210° C for 45 minutes with complete destruction of strength. This is possibly due to the iron content of the tap water. Also, at the temperature of 210° C we were approaching the ignition temperature as mentioned by Buchanan (14).

The second K series was made by using deionized water in the Nobel and Wood mixing tank and running the tap water for one hour. Thus we could keep the iron content to a minimum. Also the samples were heated to 175° C. for 45 minutes. This we hoped would keep us far below the ignition temperatures of our sample as cited by Buchanan (14). After heating, it was found we had an increase in strength which is very unusual.

### 2. S. Series

The first S-series was made with ordinary tap water. It was noted that the sheets were highly colored by iron present in the water. The samples were heated to 210° C. for 45 minutes. Also it was observed that all strength was gone and the results were failure.

The second S-series was made using deionized water in the Nobel and Wood mixing tank. It was noted that color was good and white. The samples were heated at 175° for 45 minutes and good strength still remains after heating.

TABLE S-SERIES

SAMPLE	SULFITE	ASBESTOS	VI-TARD	FOLD		BRIGHTNESS	
				UNAGED	AGED 175°C 45MIN	UNAGED	AGED 175°C 45MIN
S-1	15 gm	-	-	23.5	20	79.1	67.2
S-2	15 gm	1.5 gm	-	15.5	9.3	80.2	69.1
S-3	15 gm	1.5 gm	.78 gm	10.3	2.6	80.8	69.7
S-4	15 gm	1.5 gm	1.5 gm	8.8	9.3	81.4	70.5

TABLE K-SERIES

SAMPLE	KRAFT	AQUAPEL	KYMENE	KELGIN MV SOL'N	FOLD		BRIGHTNESS		COPPER NUMBER	
					UNAGED	AGED 175°C 45MIN	UNAGED	AGED 175°C 45MIN	UNAGED	AGED 175°C 45MIN
K-1	15 gm	-	-	-	73.1	57.1	77.3	66.8	3.39	6.1
K-2	15 gm	.6 gm	.2 gm	-	6.4	7.5	74.8	62.6	2.5	6.34
K-3	15 gm	.6 gm	.2 gm	.5%	12.3	23.0	73.4	59.3	2.5	4.87
K-4	15 gm	.6 gm	.2 gm	1%	20.8	23.0	72.4	55.9	2.75	5.73

### Discussion of Data:

As noted in the procedure, the iron content seemed to have a marked effect on the degradation of the samples. It is thought that the iron, being a good conductant of heat, concentrated the heat at those places where it was present and added greatly to the degradation of the samples.

It was also noted that sample K-3 increased in strength upon heating. This was verified by its lower copper number. The reason K-3's strength increased more than K-4's was probably due to a better impregnation of the sodium alginate at a lower concentration. It is thought that the sodium alginate protected the cellulose from heat degradation and also increased bonding on heating. When Aquapel-kymene 557 was added, the chemical degradation was reduced as measured by a lower copper number. However, when the samples were heated the copper number was increased dramatically indicating a break down of the Aquapel-kymene 557 complex--thus aiding in degradation.

### Conclusion

In samples S-3 and S-4 it was noted that with 10% asbestos fiber and the antimony resin solution was still able to get good strength from these materials. Also strength was actually increased slightly after heating. This is almost unheard of in asbestos containing paper. The brightness before and after heating was increased by the use of these materials in S-3 and S-4. With more work this material may find an application to the paper cups and paper plate industry. Also there is a possibility for use in paper permanence with natural ageing.

In sample K-3 and K-4 the value of being able to increase the strength properties upon heating is of great value to electrical insulation manufactures, and also to the paper industry in general. With good strength at high temperatures, paper machines can be run at higher speeds and higher

temperature thus increasing paper production without the expense of strength.

It can be concluded from this work that there is room for more investigation with these materials. Due to a limited length of time, more data was unable to be collected. But it is recommended that more work be done to determine what happens between  $175^{\circ}\text{C}$  and  $210^{\circ}\text{C}$ .

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