## Degradation of Cellulosic Fibres in Contact with Rusting Iron

INSTANCES of rapid degradation of textile materials in industrial use have been noted, the cause of which could not be attributed to the more usual degrading agencies, that is, micro-organisms, heat, light or acids. It was significant that in each of these occurrences there was evidence that the cellulosic material had been in contact with corroding iron under damp conditions. Similar degradation was observed in laboratory experiments in which cellulosic fibres were placed in contact with a clean iron surface and kept moist, a rapid fall in tensile strength being found as corrosion proceeded. The curves in Fig. 1 show the loss in strength of cotton yarn (8's × 5) damped with distilled water (curve $A$) and with 0·02 per cent sodium chloride solution (curve $B$) when wound on polished mild steel rods and kept in a moist atmosphere. Yarn wound on glass rods and exposed under the same conditions showed no significant change of strength in the same period (curve $C$).

An explanation of the cause of this degradation follows from consideration of the generally accepted electrochemical mechanism for the corrosion of iron wetted with a neutral salt solution. According to this mechanism, a flow of current occurs between separate regions of differing potential on the iron surface, the electrode reactions being expressible as :

Anodic reaction : $Fe \rightarrow Fe^{2+} + 2e$
Cathodic reaction: $O + H_2O + 2e \rightarrow 2OH^-$
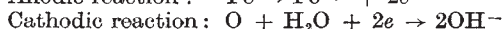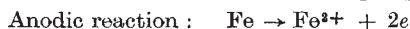
If sodium chloride is present in the solution, the cathodic and anodic products can be regarded as sodium hydroxide and ferrous chloride respectively.

When cellulosic fibres are saturated with sodium hydroxide solution and exposed to the air, oxygen is consumed and the cellulose molecules are broken down. This reaction, which is the basis of the pulp 'ageing' process in viscose manufacture, has been studied fairly extensively[1,2], and it has been shown, and confirmed in this laboratory, that two of the main factors affecting the rate of cellulose degradation are : (a) the concentration of sodium hydroxide in the fibres ; (b) the concentration of certain metals in the fibres, for example, iron, cobalt, nickel, etc., which are catalysts for the reaction. Moist cellulosic fibres in contact w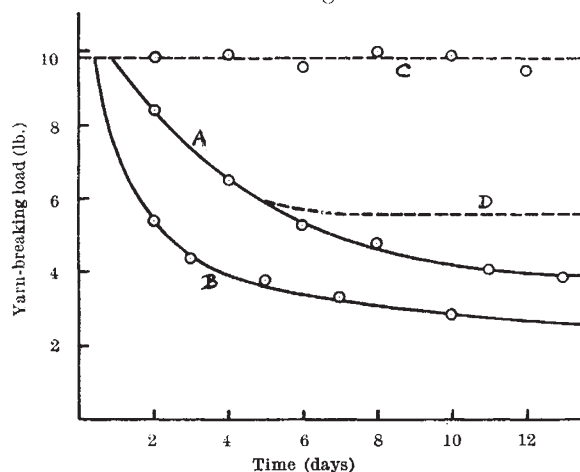ith rusting iron will thus be in an environment highly conducive to oxidative degradation by virtue of (a) the presence of local concentrations of alkali and (b) the presence of iron ions, which are active catalysts for the oxidation.

This explanation is supported by the following observations.

(1) Yarn wound closely on a rusting iron rod acquired a mottled pattern of rust-stained and unstained zones, the stained parts having a neutral and the unstained an alkaline reaction. Degradation of the fibres was most severe at the junctions of these zones.

(2) Yarn wetted with salt solution degraded faster than that wetted with distilled water. This is consistent with a difference in the level of alkali concentration reached in the cathodic zones resulting from the difference in conductance (and thus the rate of $OH^-$ ion production) and in the availability of sodium ions to balance the hydroxyl ions. The results with distilled water suggest that enough alkali metal ions were present as impurities in the yarn (which was not specially purified) to produce sufficiently high local concentrations of hydroxide to promote the degradation observed.

(3) Yarn removed from rusting iron after losing 40 per cent strength, and thereafter kept moist, suffered no significant further loss in strength (curve $D$). Removal of the fibres from the alkali-generating sources on the iron surface would be followed by a fall in the local alkali concentrations by diffusion and reaction with iron ions to form rust, and the rate of cellulose oxidation would diminish rapidly.

(4) The strength of cotton yarn, saturated with a thick aqueous slurry of finely divided sulphur, was found to be unimpaired after 28 days in contact with an iron rod in a moist atmosphere. Under these conditions, in confirmation of Farrer and Wormwell's observations[3], very rapid and severe corrosion of the iron occurred and the yarn became heavily impregnated with a black corrosion product. In this system it may be assumed that the sulphur takes the place of oxygen in the normal cathodic reaction, sulphide ions being formed instead of hydroxyl ions, thus :

$$S + 2e \rightarrow S^{2-}$$

Since no alkalinity is produced, no oxidative breakdown of the cellulose would occur.

(5) Two samples of cotton yarn, the first impregnated with 5 per cent magnesium sulphate + 0·1 per cent sodium chloride, and the second with 0·1 per cent sodium chloride only, were damped and exposed on iron rods. The iron corroded rapidly in both cases, the rate being slightly less in the presence of magnesium sulphate, but while the yarn containing only sodium chloride degraded rapidly, the yarn treated with magnesium sulphate showed no loss in strength after 23 days. The precipitation of hydroxyl ions as magnesium hydroxide evidently prevented the development of sufficient alkalinity to promote oxidation.

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Fig. 1. $A$, yarn on iron, wetted with distilled water ; $B$, yarn on iron, wetted with 0·02 per cent sodium chloride solution ; $C$, yarn on glass, wetted with distilled water ; $D$, yarn removed from iron

[1] Davidson, G. F., *J. Textile Inst.*, **23**, 95 (1932).
[2] Entwistle, D., Cole, E. H., and Wooding, N. S., *Text. Research J.*, **19**, 527, 609 (1949).
[3] Farrer, T. W., and Wormwell, F., *Chem. and Ind.*, 106 (1953).