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A Laboratory Investigation into the Possible use of Acetylation

For

(i) The Elimination of the Discolouration of Phenol-Formaldehyde Resin Treated Cotton Fabric and

(ii) The Prevention of Subsequent Discolouration on Exposure to Light

by

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A LABORATORY INVESTIGATION INTO THE POSSIBLE USE OF ACETYLATION FOR (i) THE ELIMINATION OF THE DISCOLOURATION OF PHENOL-FORMALDEHYDE RESIN TREATED COTTON FABRIC AND (ii) THE PREVENTION OF SUBSEQUENT DISCOLOURATION ON EXPOSURE TO LIGHT

by R. E. HORN

ABSTRACT

Samples of phenol-formaldehyde resin finished cotton fabric when acetylated were found to be less discoloured than unacetylated fabric. The acetylation produced a gradual loss in tear strength and a small loss in resistance to flat abrasion as the acetyl content was increased, but the crease recovery angle and handle were found to be unaffected. Upon exposure to light the acetylated samples discoloured less quickly than the unacetylated fabric.

INTRODUCTION

"The omnipotent aminoplasts. With these resins, today's textile chemical innovators are still blazing new trails", wrote Richardson[1] recently. Ever since the early 1930's aminoplast resins and urea formaldehyde in particular have been used almost exclusively for crease-resist/durable-press finishing of cellulosic fabrics. It was Marsh and his co-workers at Tootal Broadhurst Lee who pioneered the early work[2,3,4], and the first patents were filed in 1926. However, at that time they were more interested in phenolic-formaldehydes because these resins had superior wash fastness properties compared to urea formaldehyde. Unfortunately, however, the phenolic resins are discoloured and this was found to intensify on exposure to light, the problem was never solved. Marsh *et al* instead shifted their emphasis to the colourless urea-formaldehyde resins and with acknowledged success. In fact one writer[1] recently enthusiastically dubbed Marsh "the father of creaseproof cotton". During the post war years, however, a considerable amount of research was undertaken to find new resins with properties superior to urea-formaldehyde. Scores of different aminoplasts were patented and manufactured[5,6] and some of the more popular of these today are derivatives of urea-formaldehyde, melamine formaldehyde and ethylene urea[7]. Even after almost 50 years, however, the 'old original' urea-formaldehyde is still widely used and manufactured by dozens of textile firms[1].

Although the amount of time and effort spent on developing new and improved aminoplasts has been considerable the same cannot be said of the phenolics. Writing in 1962. Marsh[5] stated that "for more than 30 years, the application of the phenol-formaldehyde resins as textile finishing agents remained without attention; Chance, Perkerson and McMillan (1959)[8] repeated the work of Foulds, Marsh and

Wood, confirming the original observations". Apart from this work the only other recent study was undertaken at SAWTRI where a novel method[9] was proposed for the crease-resist finishing and dyeing of cotton fabric. Briefly, a cotton fabric is treated with a phenolic-formaldehyde resin and then dyed by immersion in a solution containing a diazonium salt which couples to the resin. Fabrics treated thus were found to have satisfactory crease-resist and tensile properties together with a good handle. The colours varied from yellow to red and the fabrics had excellent properties of fastness to washing and dry rubbing.

Another textile application of phenol-formaldehyde has been in the field of synthetic fibres. Phenolic fibres, produced by the phenol-formaldehyde reaction, have been manufactured in both the U.S.A. and Japan[10]. ®Kynol, for example, is a lightweight fibre which, because it has a moisture regain close to that of cotton, produces garments which are comfortable to wear. But its main advantage over other synthetic fibres (such as polyamide and polyester) is that it does not melt, burn or shrink in a flame of temperature up to 2 500°C. A phenolic fibre, when spun, has a characteristic yellow-orange colour but it is claimed that the fibre can be 'bleached' white by acetylation[11,12,13]. As a cotton fabric treated for a crease-resist finish with phenol-formaldehyde is also discoloured, it seemed reasonable to consider whether the discolouration could be removed by acetylation. It is quite possible also that acetylation could prevent further discolouration on exposure of the fabric to light. The acetylation of cellulosic fabrics has been known for some time and processes devised by the USA Agricultural Research Service have been adapted for commercial operation[14].

The object of this study therefore was to prepare a series of phenol-formaldehyde resin-treated cotton fabrics and to acetylate them, using available methods, to varying percentages of acetyl content. The colour of the fabrics was then measured and also after exposure to light and compared with an unacetylated sample. The effect of acetylation on the physical properties of the resin-treated samples was also assessed.

EXPERIMENTAL

A plain weave, bleached, all-cotton fabric of the following specifications was used throughout this study. The fabric density was 131g/m^2 with a sett of 33,5 ends per cm and 22,8 picks per cm. The yarn linear densities were warp 17,7 tex Z 879 and weft 24,5 tex Z 859. Samples of fabric 30 cm x 30 cm were used for each treatment.

The phenol-formaldehyde resin was prepared by boiling under reflux for 15 minutes, phenol (25 g), 40 *per cent* formaldehyde (22 g) and 20 *per cent* NaOH solution (4 g). This solution was allowed to cool to room temperature after which it was diluted to 90 g with water. The solution was padded (3 dips, 3 nips), at 70 *per cent* expression, onto samples of cotton fabric by means of a Benz pad mangle, dried for 3 min at 100°C and then cured for 5 min at 150°C. The samples were soaped at the boil for 10 min in a solution containing ® Ultravon HD (0,2 *per cent*) and Na_2CO_3 (0,2 *per cent*) after which they were rinsed and dried.

The resin finished samples were acetylated in an Ahiba laboratory dyeing machine. The fabrics were run for one hour in glacial acetic acid (250 ml), at 23°C, removed and passed through a Benz pad mangle at 70 *per cent* expression. They then entered an acetylating solution of glacial acetic acid (85 *per cent*), acetic anhydride (15 *per cent*) and perchloric acid (0,15 *per cent*), also at 23°C and treated for various periods of times. Finally the samples were rinsed in cold water, soaped at the boil for 10 min in a solution containing 0,2 *per cent* ® Ultravon HD, and then thoroughly rinsed.

The percentage acetyl content of the fabrics was estimated by the method of Eberstadt modified by Genung and Mallet[15]. Portions of fabric were ground in a Wiley mill through a 20 mesh screen and approximately 0,5 g samples were saponified for 16 hrs at room temperature in 50 ml of a solution containing 0,25 N NaOH in 95 *per cent* ethanol. The excess alkali was titrated with 0,25 N HC1 and from the titre the percentage acetyl content was determined.

The crease recovery angle of the fabrics was measured at 65 *per cent* RH and 20°C on a Monsanto Wrinkle Recovery Tester. The flexural rigidity was determined by the cantilever method. The tear strength was measured on an Elmendorf Tear Strength Tester and the bursting strength on a Mullen Tester. Finally the resistance of the fabrics to flat abrasion was determined on a Martindale Abrasion Tester with a headweight of 800 g.

The stability of the "colour" of the fabrics to light was assessed by mounting samples at a distance of 40 cm from a mercury-tungsten fluorescent lamp. Also mounted with the samples were blue wool lightfastness standards 1 to 8. After various periods of time the fabrics were removed and their tristimulus values, X Y Z, were measured on a Harrison-Shirley Digital Colorimeter. From these values were calculated, using the CIELAB colour difference formula[16], ΔE (the colour difference), ΔL (the difference in lightness), ΔC (the difference in chroma) and $H_1 - H_0$ (the difference in hue). The time of exposure of the samples to light was estimated by examining the blue standards and noting the number of the standard which just showed appreciable fading.

RESULTS AND DISCUSSION

Resin-treated samples acetylated for 0,75 hr, 2,2 hrs, 4,5 hrs and 13 hrs, were found to have acetyl contents of 1,7, 2,1, 3,2 and 5,8 *per cent* respectively. The physical properties of these fabrics were measured and these are shown in Table I. As can be seen acetylation had very little effect on the crease recovery angles or bending lengths, all the results for the acetylated samples being reasonably close to one another and to the unacetylated sample. The bursting strengths of all the acetylated samples, on the other hand, were higher than the unacetylated fabric while a significant loss in tear strength was observed with increasing acetyl content.

TABLE I

SOME PHYSICAL PROPERTIES OF ACETYLATED, PHENOL-FORMALDEHYDE RESIN-TREATED COTTON SAMPLES

% Acetyl Content	Monsanto Crease Recovery Angle (W+F) ^{0}	Bursting Strength kNm^{-2}	Tear Strength (Mean W+F) N	Bending Length cm	Martindale Flat Abrasion % loss in mass after 2500 cycles
Untreated	170	618	7,8	1,84	1,7
0	240	623	7,3	1,83	1,7
1,7	245	691	6,4	1,88	1,7
2,1	240	662	6,4	1,88	1,7
3,2	246	686	5,4	1,95	1,9
5,8	240	672	5,3	1,75	3,1

For the flat abrasion there was little difference in the percentage loss in mass of the samples with an acetyl content of up to 2,1 *per cent* but beyond this the mass loss increased. It would appear therefore that overall, acetylation does have a significant effect on the physical properties of the fabrics. Although the crease recovery angle and the handle appeared to be unaffected, both the tear strength and to a lesser extent the resistance to flat abrasion, fell with increasing acetyl content.

The effect of acetylation on the colour of the resin-treated fabrics is shown in Table II. It can be seen that as the acetyl content increased so ΔE (the colour

TABLE II

THE EFFECT OF ACETYLATION ON THE COLOUR OF PHENOL-FORMALDEHYDE RESIN-TREATED SAMPLES

% Acetyl Content	ΔE	ΔL	ΔC	$H_1 - H_0$
1,7	7,61	5,90	-0,60	17,1^0
2,1	8,59	6,23	-0,69	21,2^0
3,2	9,89	7,69	0,56	21,6^0
5,8	16,76	12,38	5,73	29,8^0

Where $L_0 = 67{,}6$, $C_0 = 12{,}6$ and $H_0 = 52^0$ (resin-finished unacetylated fabric)

difference), compared to an unacetylated resin-treated sample, increased. However, ΔE is only a measure of the colour difference and gives no indication in real terms of what the difference is due to; from ΔE therefore were calculated ΔL, ΔC and $H_1 - H_0$. ΔL shows that as the acetyl content was increased so the fabrics became lighter in colour. ΔC indicates that there was very little difference in chroma between the unacetylated sample and the fabrics with acetyl contents of 1,7, 2,1 and 3,2 *per cent* although the 5,8 *per cent* did have a higher chroma. $H_1 - H_0$ reveals that the samples were moving away from the 'natural' orange-red colour ($H_0 = 52°$) of the unacetylated fabric to become less red, more yellow as the acetyl content increased. It can be concluded therefore that acetylation does have an effect upon the colour of a phenol-formaldehyde resin-treated cotton fabric, in that the fabrics become lighter and less red, more yellow with increasing acetyl content.

This, however, is only part of the problem and it was necessary next to assess whether acetylation could prevent or reduce the discolouration of the resin when exposed to light. The results are shown in Fig. 1 to 4. It must be noted that in order to observe the behaviour of an unacetylated sample, ΔE, ΔL, ΔC and $H_1 - H_0$ have been calculated with respect to the original untreated fabric (L_0 = 94,0, C_0 = 2,8, H_0 = 111,9°).

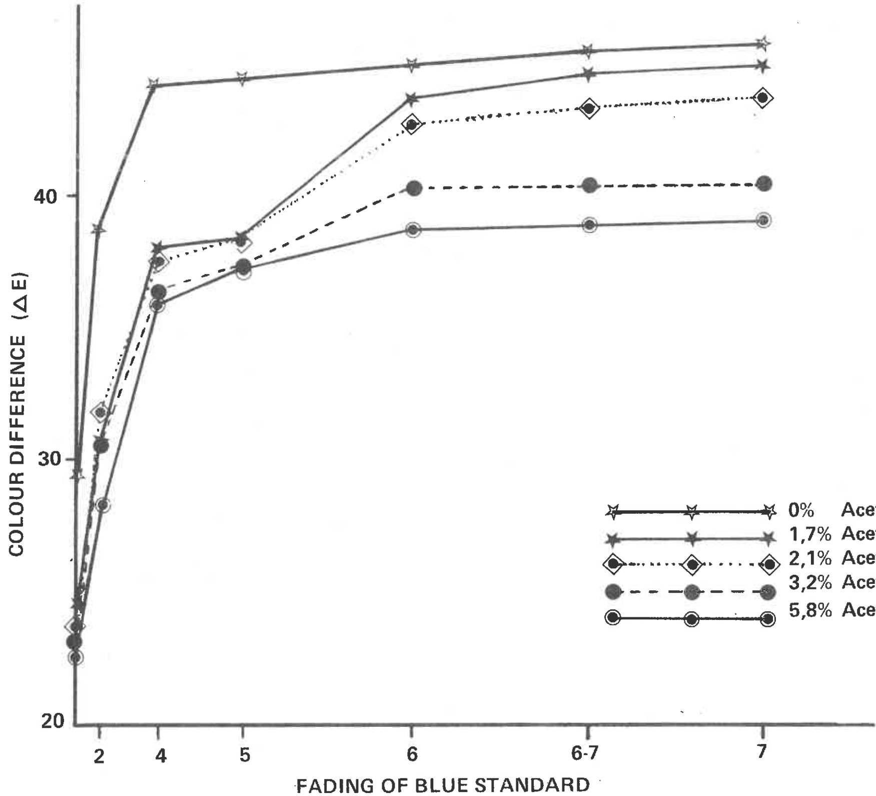

FIGURE 1

The Colour Difference (ΔE) between Untreated Cotton and Resin-treated and Acetylated Fabrics

Figure 1 shows that in all cases a rapid increase in ΔE, the colour difference compared to the original white fabric, was observed up to the commencement of fading of blue standard 4 and then after that each sample behaved slightly differently. For the sample with an acetyl content of 0 *per cent* little increase in ΔE occurred after this point but with the 1,7 *per cent* acetyl, ΔE continued to rise and almost reached the level of the unacetylated fabric. As the acetyl content of the fabric was increased so the increase in ΔE after blue standard 4 became less and in fact the sample with an acetyl content of 5,8 *per cent* showed the smallest increase. In all cases also little to no change was observed in ΔE after the start of fading of blue standard 6.

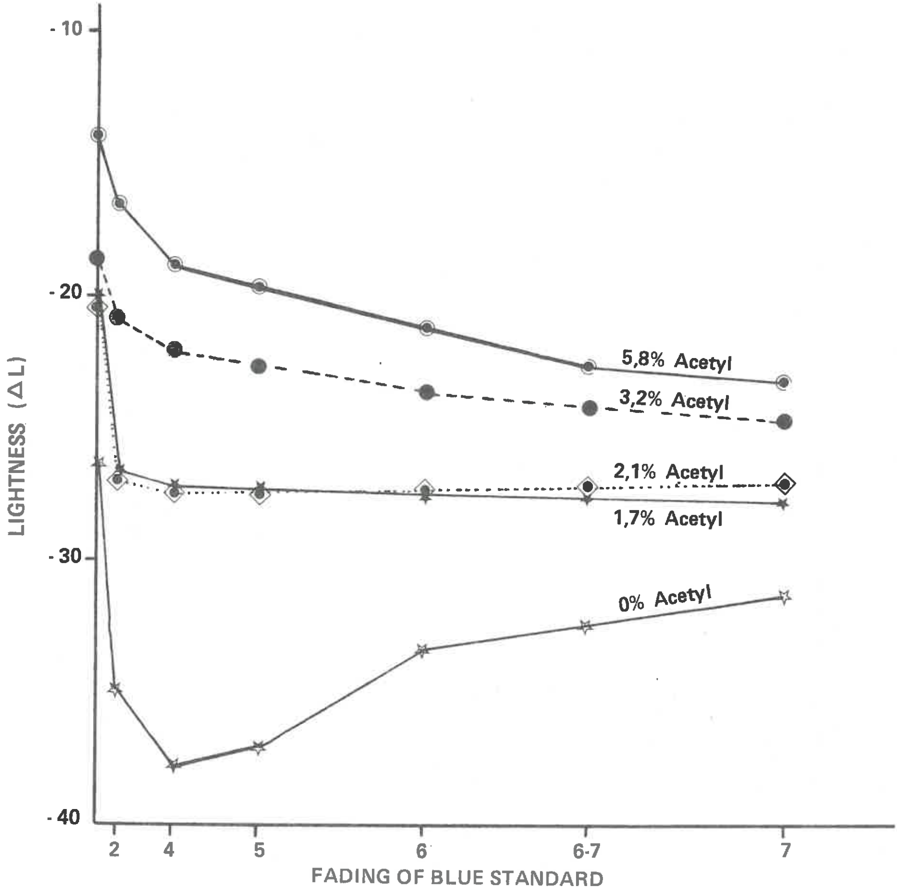

FIGURE 2

The Difference in Lightness (ΔL) between Untreated Cotton and Resin-treated and Acetylated Fabrics

In Fig. 2 is shown the plot of ΔL (lightness) against time of exposure. It can be seen that the unacetylated sample became duller very quickly, shown by the rapid fall in ΔL, but after the fading of blue standard 4, began to become gradually lighter. The 1,7 *per cent* and 2,1 *per cent* acetyl samples rapidly went duller but after blue standard 2 had faded there was little change. Both the samples with acetyl contents of 3,2 *per cent* and 5,8 *per cent* became duller more slowly but were much lighter than the unacetylated sample after blue standard 7 had faded.

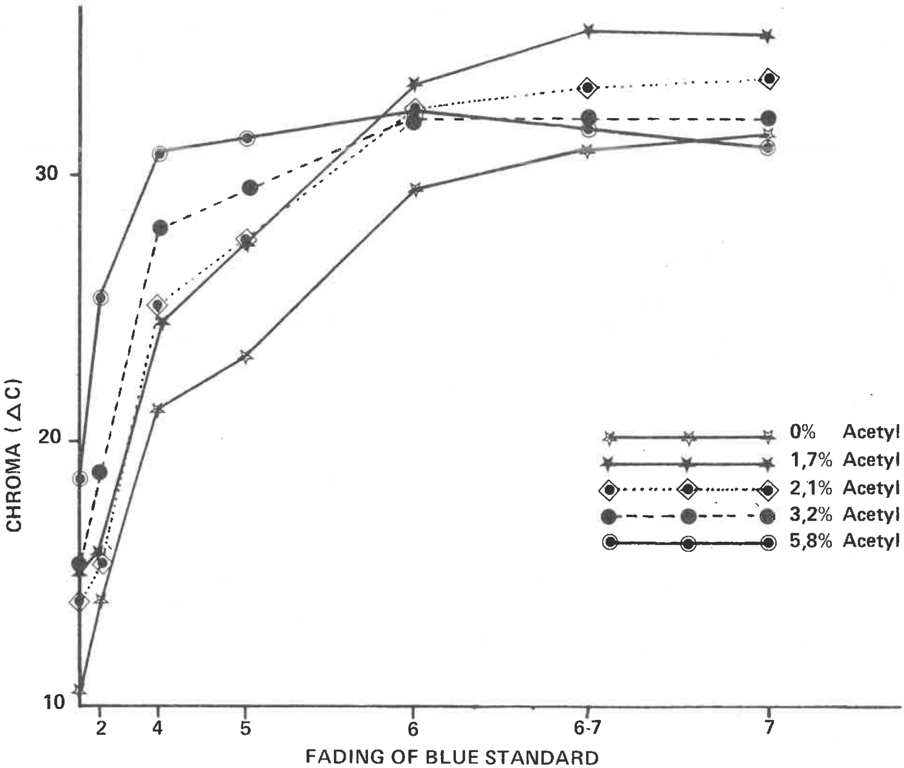

FIGURE 3

The Difference in Chroma (ΔC) between Untreated Cotton and Resin-treated and Acetylated Fabrics

Fig. 3 indicates the change in ΔC (chroma) with time and it can be seen that all the samples followed a similar pattern. In all cases a rapid increase in ΔC was observed but after the commencement of fading of blue standard 4 the increase became more gradual to blue 6–7 after which there was little change. After blue standard 7 had faded the sample with an acetyl content of 1,7 *per cent* had the highest value for ΔC and the one with 5,8 *per cent* the lowest, the unacetylated sample lying close to the latter.

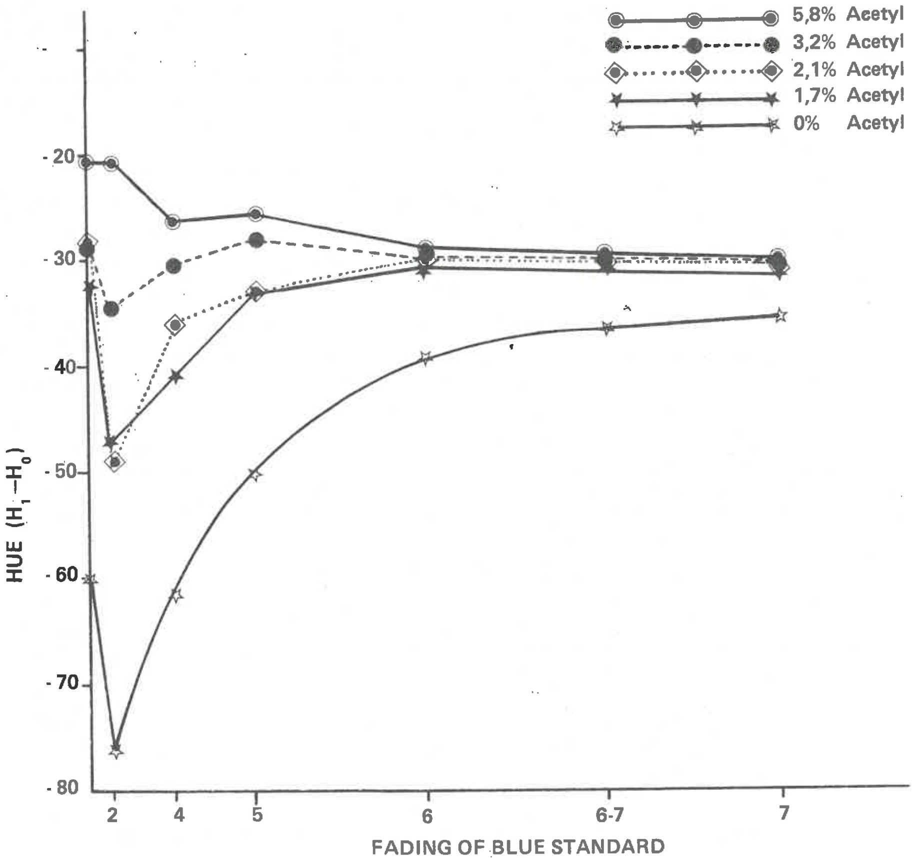

FIGURE 4

The Difference in Hue (H_1-H_0) between Untreated Cotton and Resin-treated and Acetylated Fabrics

Fig. 4 shows the change in hue (H_1-H_0) with time. It can be seen that the unacetylated sample rapidly went redder but after blue standard 2 had faded became less red, more yellow and in fact finished with a larger value for H_1-H_0 than before exposure. The samples with an acetyl content of 1,7 *per cent* and 2,1 *per cent* also followed a similar pattern, both rapidly became redder and then yellower but unlike the unacetylated sample, they returned roughly to their original values of H_1-H_0. The 3,2 *per cent* and 5,8 *per cent* samples behaved a little differently giving a much more gradual fall in H_1-H_0. Both rose slightly between blue standard 4 and 5, but fell again and after blue standard 6 little change was observed.

At blue standard 7 all the acetylated samples had larger values for $H_1 - H_0$ than the unacetylated fabric indicating that they were less red.

Finally, it was concluded from the results shown in Fig. 1 to 4 that acetylation did reduce the discolouration of the samples on exposure to light and that the greater the acetyl content, the greater the reduction.

SUMMARY

Samples of phenol-formaldehyde resin finished cotton fabric were acetylated to acetyl contents of 1,7, 2,1, 3,2 and 5,8 *per cent*. They were found to be lighter and less red in colour than unacetylated fabrics, and the colour difference increased with increasing acetyl content. The treatments had little effect on the crease recovery angle or the handle of the fabrics but the samples suffered a gradual fall in tear strength and a small loss in resistance to flat abrasion. When the fabrics were exposed to light acetylated samples with increasing acetyl content were slower in becoming duller and redder than unacetylated fabric, the difference increasing with increasing acetyl content.

ACKNOWLEDGEMENTS

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THE USE OF PROPRIETARY NAMES

Products marked ® are registered trade names. The fact that chemicals with proprietary names have been mentioned in this investigation in no way implies that SAWTRI recommends them or that there are not others of equal or greater merit.

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