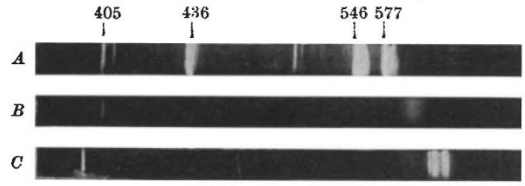
## Distribution of Fluorescence Excitation of Bivalent Europium in Calcium Fluoride and of Bivalent Samarium in Calcium Sulphate

IN an earlier communication[1], it was mentioned that prolonged treatment of rare earth preparations with short-wave ultra-violet radiations produces an effect similar to that obtained with radium rays.




The accompanying reproductions show the effect very distinctly. In all cases the same preparation of calcium sulphate with $10^{-3}$ samarium was used. The photographs were taken on material sensitized in each case for the required range. *A* shows the untreated preparation reflecting the light of the mercury vapour lamp. *B* and *C* were taken after the preparation was treated for 30 hours with light of the wave-length 240 mμ. The bands then were excited by illuminating with filtered ultra-violet. In *C* at the left of the band which extends from 689 mμ to 734 mμ also the band at 630 mμ can again be recognized as in *B*.

The mercury lines marked are those at 405, 436, 546, 577 mμ.

HERBERT P. ECKSTEIN.

Louisville, Ky.
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[1] NATURE, **142**, 256 (1938).

## Similarity of the X-Ray Patterns of Tanned and Mechanically Deformed Collagen Fibres

THE X-ray pattern of the collagen of animal skin has been shown[1,2] to undergo a characteristic alteration on combination of the collagen with various tanning agents. As seen in patterns produced by the ordinary technique (a mass of fibres of random orientation; unfiltered copper radiation; specimen to film distance of from two to five centimetres), this alteration consists of a remarkable diffusion of the originally sharp 'inner' ring (the side-chain spacing of 10–12 A.). The resultant diffuse halo extends clear into the central spot, and the periphery of the ring loses its original sharpness. In addition to this, the 'outer' ring (the unit backbone spacing of 2·9 A.) becomes greatly diminished in intensity, and in extreme cases disappears completely. The extent of these changes depends upon the proportion of the tanning agent combined with the collagen, the effect being more pronounced with higher tannin fixations.

It has been suggested[2,3] that they are due to a distortion of the protein grid, caused by the penetration into the grid of the large molecules or molecular complexes of the tanning agent. In agreement with this hypothesis, it is found that the greatest effect on the pattern is produced by those materials which are of relatively large molecular size and complexity, such as the natural vegetable tannins and the basic chromium salts, while substances of a simpler nature and presumably smaller molecular size produce little or no effect. Formaldehyde and certain synthetic tannins are in the latter group. An exception to this rule is apparently found in quinone, which produces an effect very similar to that of the larger tannin molecules. This may possibly be explained by a polymerization of the quinone in the alkaline solutions necessary for tannage with this substance.

We have now found that collagen which has been subjected to treatments calculated to produce mechanical deformation of the fibrils shows an X-ray pattern practically indistinguishable from that described above for tanned collagen. In carrying out these experiments, the mass of collagen fibres is first compressed into a coherent disk in a hydraulic press. This is the method we ordinarily use in preparing samples of powdered fibrous collagen for X-ray photography, and such treatment does not change the pattern in any perceptible way. Several such disks are then passed, under great pressure, between the rollers of a machine designed for rolling metal wires. The flattened disks are again reduced to the powdered state by passing through the Wiley mill, and from this powder a disk of the same weight and thickness as the original is formed in the hydraulic press. The pattern obtained from this disk, when compared on the same film with the pattern from one of the original unrolled disks, shows all the changes the characteristic features of which have been noted above. The intensity of the effect increases with additional rollings. We have also found that the same effect can be obtained merely by prolonged grinding of the collagen in the Wiley mill, where the material is subjected repeatedly to the shearing action of the knives.

These experiments have been carried out with purified collagen prepared from ox skin, and also with the tendon Achilles of the ox. Further details will be published elsewhere.

JOHN H. HIGHBERGER.

Department of Leather Research,
Institute of Scientific Research,

HAROLD J. KERSTEN.

Department of Physics,
University of Cincinnati.
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[1] Jordan Lloyd, D., *J. Int. Soc. Leather Trades Chemists*, **19**, 345 (1935).
[2] Highberger, J. H., and Kersten, H. J., *J. Amer. Leather Chem. Assoc.*, **33**, 16, 289 (1938).
[3] Jordan Lloyd, D., *J. Int. Soc. Leather Trades Chemists*, **22**, 558 (1938).

## Magnetism and Polymerization

THE graphs below refer to results we have obtained for the magnetic susceptibility of dimethylbutadiene at the commencement of polymerization. Fig. 1 is for the mass susceptibilities of samples of dimethylbutadiene distilled and sealed in nitrogen, and polymerized in the dark by heat at a temperature of 140° C. Fig. 2 is for a similar treatment of

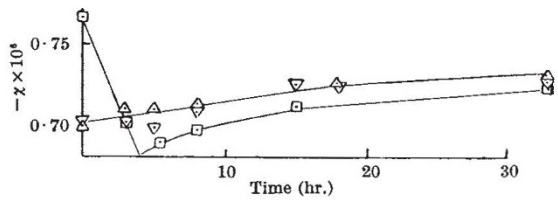


Fig. 1.

–□– Dimethylbutadiene sealed in nitrogen.
–▽– ,, + 1% benzoyl peroxide.
–△– ,, + 2% benzoyl peroxide.