

the glassy surface of the pellets and the existence of α -cristobalite in the centers. The identity of these substances was established by comparison of the data from this work with that for β - and α -cristobalite given by the A.S.T.M. index,¹ excellent agreement in line position and relative intensities being shown.

Sosman,² in his authoritative treatise on silica, states that the inversion of the high temperature form, β -cristobalite, to the low temperature form, α -cristobalite, is rapid and occurs promptly as soon as the inversion temperature range of 200 to 275° is reached. In order to substantiate our identification of the β -cristobalite pattern for the overheated catalyst, a literature search was made and two other reported instances in which β -cristobalite had been identified in room temperature samples were found: in opals^{3,4} and in glassy matrices containing silica.⁴ In the latter publication this phenomenon was attributed to the prevention of inversion by the glassy matrix in which the crystals of β -cristobalite existed. Sosman^{2,5} has denied the possibility of maintaining the beta structure by quenching but⁵ has kept open the possibility that in a glass this might occur and asked for further study.

Our results are of interest because the cristobalite in the glassy surface of the fused clay catalyst pellets was shown to be the beta form while in the non-glassy interior, complete inversion to the alpha form had taken place. This provides an excellent confirmation of Greig's⁴ contentions that the high-low inversion of cristobalite may be restrained and the high temperature form, β -cristobalite, may exist indefinitely at room temperature when the crystals of cristobalite are formed in a glassy medium. At the same time the results on the non-glassy centers are in agreement with Sosman's contention that the transformation to the alpha form cannot be delayed by quenching, if now this statement is qualified to apply to the changes occurring in a non-enclosing solid medium. As demonstrated by Greig,⁴ when adhesion between enclosing medium and cristobalite crystal is broken, then inversion to the low temperature form takes place readily. Furthermore, from his results, it appears that once the α form has been developed, cristobalite may be taken up and down through the high-low inversion point with rapid transformation into the phase expected in complete accord with Sosman's statement.

It may be of significance to researchers in the field of ceramics to note that the diffraction patterns of both α - and β -cristobalite showed practically the same extent of line broadening. From the information that line broadening is present, it

is possible to fix an upper limit to the crystal size of the cristobalites at 10^{-5} cm. Since the lines are only moderately broadened by comparison with sharp diffraction lines of the other phases present it is estimated that the crystal size lies between 5×10^{-6} and 10^{-5} cm.

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Crystallization of Triacetin

BY BERNARD HANCOCK, DONALD M. SYLVESTER AND SYLVAN E. FORMAN

Triacetin has been reported to form a glass at -78 and at -60° .¹ We have observed triacetin to crystallize at $+3.2^\circ$.

A tank car of impure triacetin which had been shipped a long distance in cold weather was received with the contents partly solidified. Some of this slush was kept overnight in a refrigerator at $+5^\circ$, but the solids had melted before morning.

The melt would not crystallize when cooled with dry ice or with an ice and salt mixture, but a portion diluted with an equal volume of absolute ethyl alcohol was crystallized readily by cooling to about -10 or -15° . Several such portions were crystallized on that day and some crystals were preserved in an ice and salt mixture.

On subsequent occasions, crystallizations of triacetin samples were induced by seeding. However, no crystals could be obtained without this aid.

A sample of triacetin was distilled at 130.5° (7 mm.). It had n_D^{20} 1.4288 and gave saponification equivalents of 72.42 and 72.35 (theory 72.70). Five small portions were cooled to about -15° and the first one was seeded with triacetin. This tube was used to seed the second tube, the second to seed the third, and so forth. This procedure was carried out to prevent impurities from being transferred by the seed crystals. Finally about 10 ml. of pure triacetin in a shielded tube was cooled to about -15° and seeded from the fifth tube. The temperature rose to $+3.2^\circ$ (cor.) where it remained until all of the solid melted.

The triacetin was converted into glycerol and ethyl acetate with ethyl alcohol and a trace of sulfuric acid. The glycerol was vacuum steam distilled. It was 98.5% glycerol by acetylation and 1.3% water by Karl Fischer titration; n_D^{20} 1.4698.

The ethyl acetate was purified by extraction with water followed by rectification. It distilled at 77° and was 99.3% pure by saponification.

(1) "Beilstein," Vol. II, first supplement, p. 70; second supplement, p. 161.

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Alpha and Beta Schardinger Dextrin Nitrates

BY N. S. GRUENHUT, M. L. CUSHING AND G. V. CAESAR

French and Rundle¹ have accurately determined by X-ray diffraction and crystal density measurements the molecular weights of the α and β -Schardinger dextrans. The α -dextrin was shown to consist of six, and the β -dextrin of

(1) French and Rundle, THIS JOURNAL, 64, 1651 (1942).

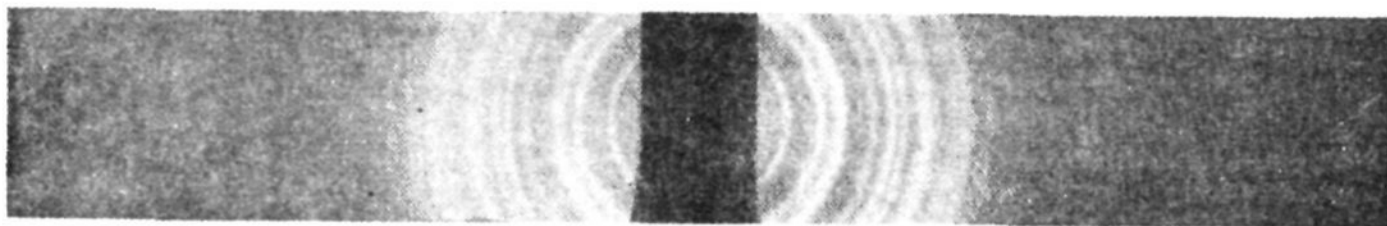
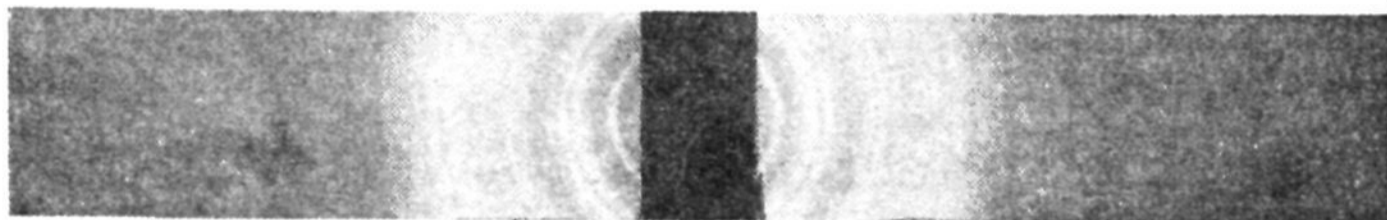
(1) First Supplement to the card file of X-ray diffraction data published by the American Society for Testing Materials, 1944.

(2) R. B. Sosman, "Properties of Silica," A. C. S. Monograph Series 37, Reinhold Publishing Corp., New York, N. Y., 1927, p. 126.

(3) I. Levin and E. Ott, THIS JOURNAL, 54, 828 (1932).

(4) J. W. Greig, *ibid.*, 54, 2846 (1932).

(5) R. B. Sosman, *ibid.*, 54, 3015 (1932).

Fig. 1a.—Schardinger α -dextrin nitrate.Fig. 1b.—Schardinger β -dextrin nitrate.

seven glucose residues. During the course of recent molecular weight determinations of completely nitrated starches and dextrans by means of the Barger isopiestic method² we decided to check the Barger technique on nitric esters of the crystalline Schardinger dextrans, compounds previously described only once.³

We were able to nitrate without difficulty the Schardinger α and β -dextrans, employing nitrogen pentoxide in chloroform in the presence of sodium fluoride according to a method previously described.⁴

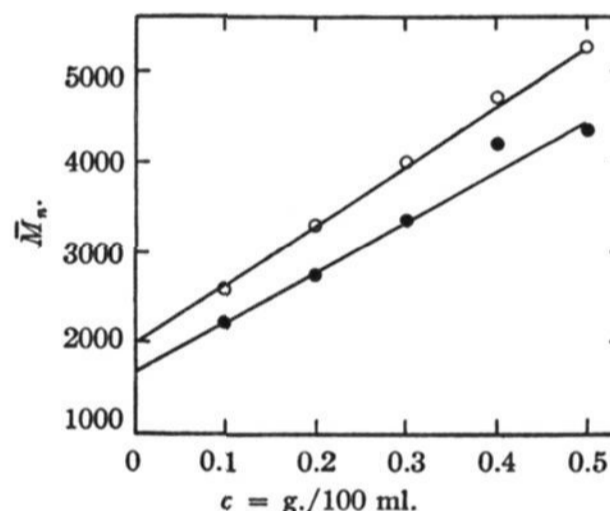
Proof of the crystalline character of these Schardinger dextrin nitric esters is attested by the photographs (Fig. 1) of their X-ray powder patterns.⁵

The derivation $c \rightarrow 0$ of number average molecular weights, determined by the Barger method,² is shown graphically in Fig. 2. Values of ca. 1,700 for the α -dextrin nitrate and 2,000 for the β -nitrate were obtained. The observed nitrogen contents were 13.61 and 13.52%, respectively.⁶ From these nitrogen values the calculated molecular weights are 1,728 and 2,009, respectively, assuming six and seven glucose residues. Complete nitration of Schardinger dextrans should yield 14.14% N. The observed degree of nitration is lower than anticipated from previous experience with starches and dextrans under similar conditions,⁴ and is attributed tentatively to steric hindrance in a ring structure.

Intrinsic viscosities, $[\eta] = \lim_{c \rightarrow 0} \eta_{sp}/c$, were determined in ethyl acetate solution. The $[\eta]$ of the α -dextrin nitrate was 0.048, of the β -dextrin nitrate 0.080.

The Schardinger dextrin nitrates failed to exhibit a sharp melting point. The α -dextrin nitrate

began to decompose slowly at 167–168°, the β -nitrate at 184–186°.

Fig. 2.—Schardinger dextrin nitrates; derivation of $\bar{M}_{nc \rightarrow 0}$ in ethyl acetate: ●, α ; ○, β -dextrin.

Experimental

Preparation of Schardinger Dextrin Nitrates.—A chloroform solution of 250 ml. containing 47.3 g. of nitrogen pentoxide was cooled to -15° . Ten grams of sodium fluoride was added and the dispersion mechanically agitated during the slow addition of 10 g. of dried crystalline Schardinger dextrin.⁷ The temperature was allowed to rise slowly to 8° during a reaction period of one hour. The nitrated dextrin, admixed with sodium fluoride, was removed by filtration, purified and stabilized according to the procedure elsewhere described.⁴

Molecular Weight and Intrinsic Viscosity Determinations.—These were determined according to procedures elsewhere described.²

X-Ray Diffraction Patterns.⁵—These (Fig. 1) were obtained with a cylindrical camera of approximately 10 cm. radius using filtered copper radiation.

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(2) Caesar, Gruenhut and Cushing, *ibid.*, **69**, 617 (1947).

(3) Pringsheim, *et al.*, *Ber.*, **58**, 1889 (1925).

(4) Caesar and Goldfrank, *THIS JOURNAL*, **68**, 372 (1946).

(5) Courtesy of the Eastern Regional Research Laboratory, Phila., Pa., Phys. Chem. Sec., F. R. Senti.

(6) Nitrometer determinations by Mr. Leslie M. Redman, Organic Research Laboratory, Massachusetts Institute of Technology.

(7) Courtesy of C. S. Hudson, National Institute of Health, Bethesda, Md.