STUDIES IN THE AGEING OF CORDITES BY X-RAY DIFFRACTION

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ABSTRACT

The results of X-ray diffraction on the ageing of WM & NA cordites, particularly that of nitrocellulose, are reported. The samples studied were: (1) Relatively fresh samples (1953) (2) Naturally aged samples (stored for about 10 years), (3) Accelerated aged ones (samples kept at 70°C for 80 hours), (4) Samples kept at liquid air temperature for 5 hours, and (5) Liquid air treated samples subjected to accelerated ageing (70° C for 80 hours). Two points are important about nitrocellulose: (1) denitration and (2) formation of microcrystallites. The 'd' value of the inner most arcs in WM and AN cordites considerably decreases on natural ageing. Similar change is observed in accelerated aged sample of WM, which is cooled to liquid air temperature. These results indicate the denitration of nitrocellulose. Accelerated ageing (70° C for 80 hours) or cooling down to liquid air temperature does not result in appreciable denitration. Liquid air treatment increases the number of microcrystallites, and the break down of nitrocellulose fibres into microcrystallites favours denitration.

Introduction

Decrease in propelling power of Cordites on long storage is well known. Chemical degradation of different constituents accompanied with physical changes in the Cordite grain attribute towards this phenomena. In the present case the effect of ageing in two types of Cordites (WM and AN), particularly the changes involved in nitrocellulose, were investigated by X-ray diffraction.

EXPERIMENTAL

Composition of Cordites used in the investigation was as follows :

	WM	AN
Nitrocellulose (13·1 % N)	65·0%	56·5%
Nitroglycerin	29·5%	25·5%
Mineral Jelly	3·5%	3·5%
Carbamite	2·0%	4·5%
Dinitrotoluene	Nil	10·0%
KNO_3	Nil	0·7%
$CaCO_3$	trace	trace

X-ray patterns were taken on flat camera using Cu $K\alpha$ radiation (Ni filtered). Samples examined were: (1) Relatively fresh samples (1953), (2) Naturally aged samples (stored for about 10 years), (3) Accelerated aged ones (samples kept at 70°C for 80 hours), (4) Samples kept at liquid air temperature for 5 hours and (5) Liquid air treated samples subjected to accelerated ageing (70°C for 80 hours).

Nature of X-Ray Patterns

The characteristic fibre pattern of trinitrocellulose is never obtained in Cordites. Descriptions of patterns obtained are given in Table I. (The faint arc on the inner side of the inner most ring is spurious). 'd' values are given in Table II.

TABLE I

	W.M. Cordite					A. N. Cordite			
	Fresh Sample PI	After Natural Ageing PII	After Accelerated Ageing PIII	Cooled to liq. air temp. PIV	Acc. ageing after cooling PV	Fresh Sample PVI	After natural ageing PV II	After acc. ageing PVIII	Cooled to liq. air temp. PIX
Low angle Scattering ..	Very smal	Weak but recognis-able	Large	Large	Uncertain	Very small	Present	Present	Large
Inner ring	Diffuse Broad band	Arcs on diffuse broad band	Arcs on broad diffuse band	Arcs on diffuse broad band	Arcs on diffuse broad band	Arcs on diffuse broad band	Long arcs on broad diffuse band	Strong arcs on diffuse broad band	Faint arcs on diffuse broad band
Faint diffuse band ..	Very faint	Faint	Faint	Faint	Faint	Faint	Faint	Faint	Faint
Sharp Intense ring ..	Ring	Arcs	Ring	Ring	Ring	Arcs	Arcs	Ring	Arcs
Broad diffuse band ..	Diffuse band	Diffuse band	To rings on diffuse band	Diffuse band	Two rings on diffuse band	Diffuse band	Two rings on broad band	Ring on broad band	Two rings on broad band
Outer rings	Absent	Absent	Absent	Absent	Absent	Present	Present	Present	Present
Pattern as a whole ..	Intensity low	Intensity low	Intensity high	Intensity high	Intensity high	Intensity high	Intensity high	Intensity high	Intensity very high
Back ground Scattering ..	Very small	Very small	Large	Very small	Very large	Small	Larger than in PVI	Larger than in PVII	Very large

TABLE II

'd' Values in A°

	W. M. Cordite					A. N. Cordite			
	Fresh Sample	After Natural Ageing	After Acc. Ageing	After cooled to liq. air. temp.	Acc. ageing after cooling	Fresh Sample	After Natural ageing	After acc. ageing	After cooling to liq. air. temp.
Inner arcs	7·47*	6·75	7·13	6·96	6·70	6·98	6·62	6·94	7·00
Faint diffuse band ..	4·62	4·62	4·78	4·58	4·62	4·82	4·63	4·85	4·63
Sharp ring	4·16	4·18	4·17	4·16	4·17	4·18	4·17	4·17	4·16
Broad Diffuse band ..	3·49	3·47	3·79 3·50	3·49	3·67 3·48	3·51	3·54 3·31	3·59 3·29	3·55 3·26

* Diameter at the middle of the band was taken.

Results

The patterns obtained closely resemble to those from nitrocelluloses containing about 12% nitrogen. There is only one sharp ring and others are diffuse. The extra outer rings in case of AN samples are due to the difference in compositions of the two Cordites. The general nature of the large angle scattering in any type of cordite shows little change after the various treatments. But there is considerable change in both low angle and back ground scattering.

The diffuse nature of arcs and rings does not make 'd' values particularly reliable. These values only serve as indicators of variations. The 'd' value of the sharp ring could be fairly accurately measured and it is found to remain practically constant in all the samples. In case of both WM and AN Cordites it is seen that the 'd' value of the inner most arcs decreases considerably in naturally aged samples. Similar change in 'd' value also occurs in accelerated aged sample of WM which is cooled down to liquid air temperature. Just keeping the sample at 70°C for 80 hours or cooling down to liquid air temperature does not produce any appreciable change in 'd' value of the inner arcs.

Excepting in case of fresh samples of both AN & WM Cordites, it is found that there is definite scattering very near the primary beam which is confined to about 4° in all other samples. This scattering is found to be particularly large after accelerated ageing and after cooling down to liquid air temperature.

Discussions and Conclusion

X-ray patterns of fibres may consist of:—

(1) Fairly sharp spots or arcs.
(2) Diffuse complete rings.
(3) Some general back ground scattering.
(4) Low angle scattering consisting of,
  (*a*) discontinuous interference spots, and
  (*b*) continuous scattering near the primary beam.

The interpretation of the photograph is usually given in terms of presence of two phase systems in fibres *i.e.* crystalline and amorphous[1]. Sharp spots show the presence of crystalline regions in fibres and the general nature of pattern indicates that all the molecules in crystalline regions have one particular axis parallel to fibre axis. Arcs of increasing lengths are obtained when the alignment becomes more and more imperfect. Diffuse complete rings and the general back ground are due to scattering from amorphous part[1]. The discontinuous interference in low angle region is due to the presence of large spacings in crystals. Low angle continuous scattering is due to microcrystallites with gaps or voids between them[2—4]. When this is all round the central spot, the microcrystallites have all sorts of orientation.

Hess and Trogus [5,6] have observed that 'd' value of the innermost equatorial spot (101) of nitrocellulose falls with decrease of nitrogen percentage. In present case this spot corresponds to inner most arcs. Thus it appears that denitration has taken place in cases of naturally aged WM and AN Cordites as also when WM sample is accelerated aged after cooling down to liquid air temperature.

In WM Cordites, the fresh sample shows only one sharp arc at d, 4·16 A°. The inner ring is a broad diffuse band, indicating the presence of considerable amount of amorphous matter. The naturally aged sample shows recognisable increase in low angle scattering showing formation of microcrystallites. Accelerated aged one shows large low angle and back ground scattering, showing increase of microcrystallites as well as amorphous portion. Sample cooled down to liquid air temperature shows large low angle scattering but very small back ground scattering.

These show that large break down into microcrystals has taken place. Accelerated ageing of the cooled specimen shows both large low angle and back ground scatterings, indicating increase of microcrystallites and amorphous part. Fresh sample of AN Cordite does not show much low angle scattering. Increase of low angle scattering as well as of back ground scattering occurs in samples after natural ageing, accelerated ageing and liquid air treatment. Particularly after liquid air treatment both these increase appreciably indicating the formation of microcrystallites and increase of amorphous portion.

That is, the fresh WM Cordite (1953 sample) has comparatively high amorphous portion. On natural ageing smaller crystallites are produced accompanied with denitration. On heating to 70°C increase in microcrystallites takes place but no denitration. On cooling to liquid air temperature microcrystallites are formed but no denitration. When this sample is heated to 70°C both denitration and increase of microcrystallites take place.

Fresh AN Cordite (1953 sample) shows a little higher crystalline portion than WM. On natural ageing, denitration as well as formation of microcrystallites takes place. On both accelerated ageing and liquid air treatment no appreciable denitration occurs but large increase in microcrystallites takes place.

Low angle scattering is characteristic of microcrystallites with gaps between them. The increase in low angle scattering in these samples is taken to be due to microcrystallites of nitrocellulose, as it is known that organic polymers give rise to such scattering in dispersed state [3,7] and that there is no other substance in the specimens which may show such scattering. Thus two points arise (1) denitration and (2) formation of microcrystallites.

From the 'd' values of the inner most arcs it appears that no appreciable denitration of nitrocellulose in Cordite is produced by mere change in temperature in the range studied. But in case of WM Cordites it is observed that considerable denitration takes place when it is accelerated aged after cooling down to liquid air temperature. Since cooling down to liquid air temperature increases the number of microcrystallites, it follows that the break down of nitrocellulose fibres into microcrystallites favours denitration or denitration becomes quicker in smaller clusters than in longer fibres.

Acknowledgement

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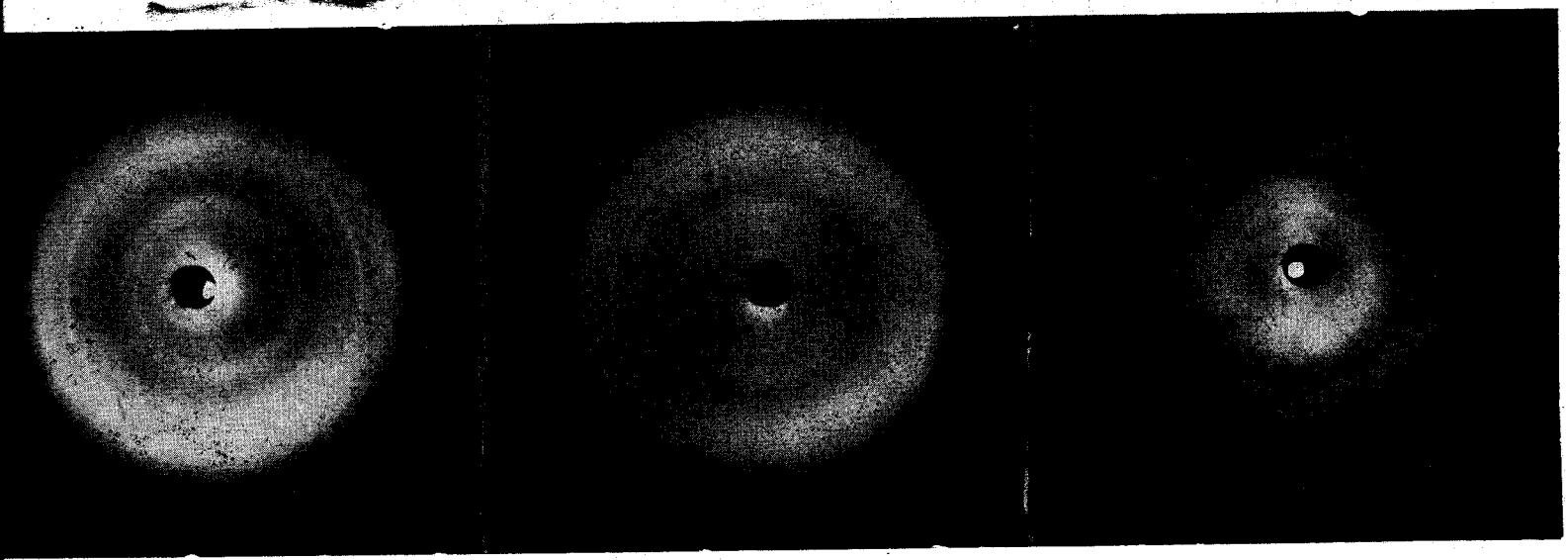
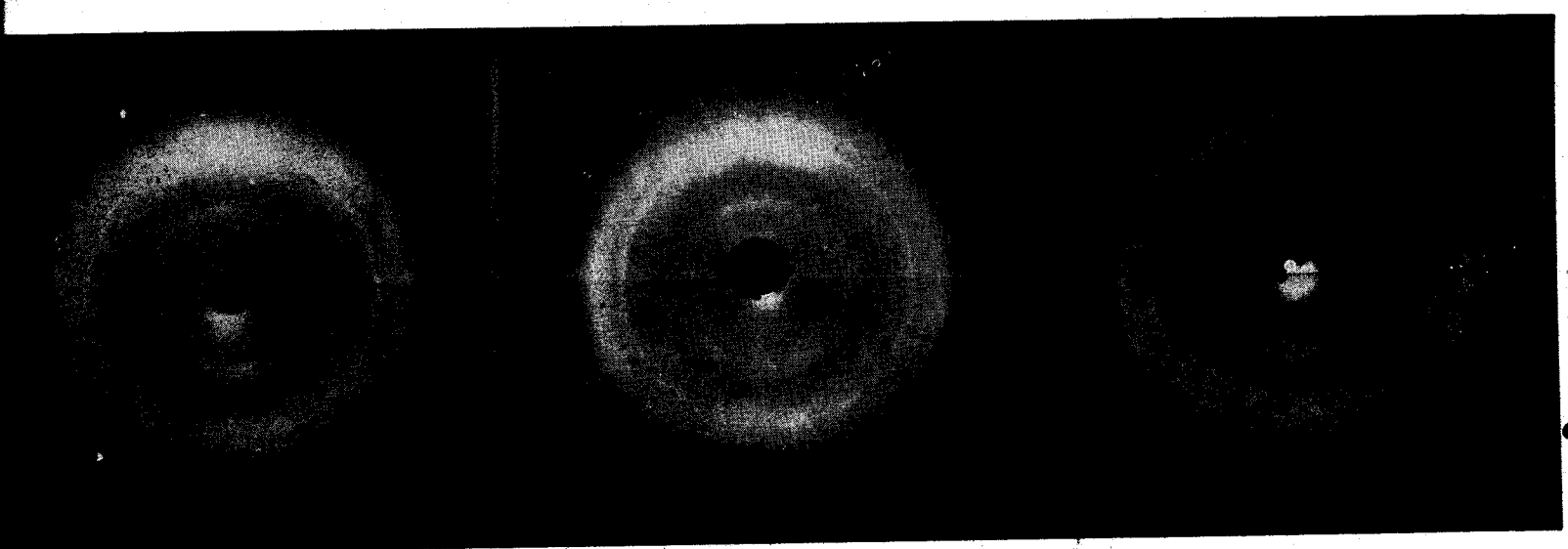


P. I.
W. M. Cordite
Fresh Sample (1953).

P. II.
W. M. Cordite
After natural ageing
(10 yrs)

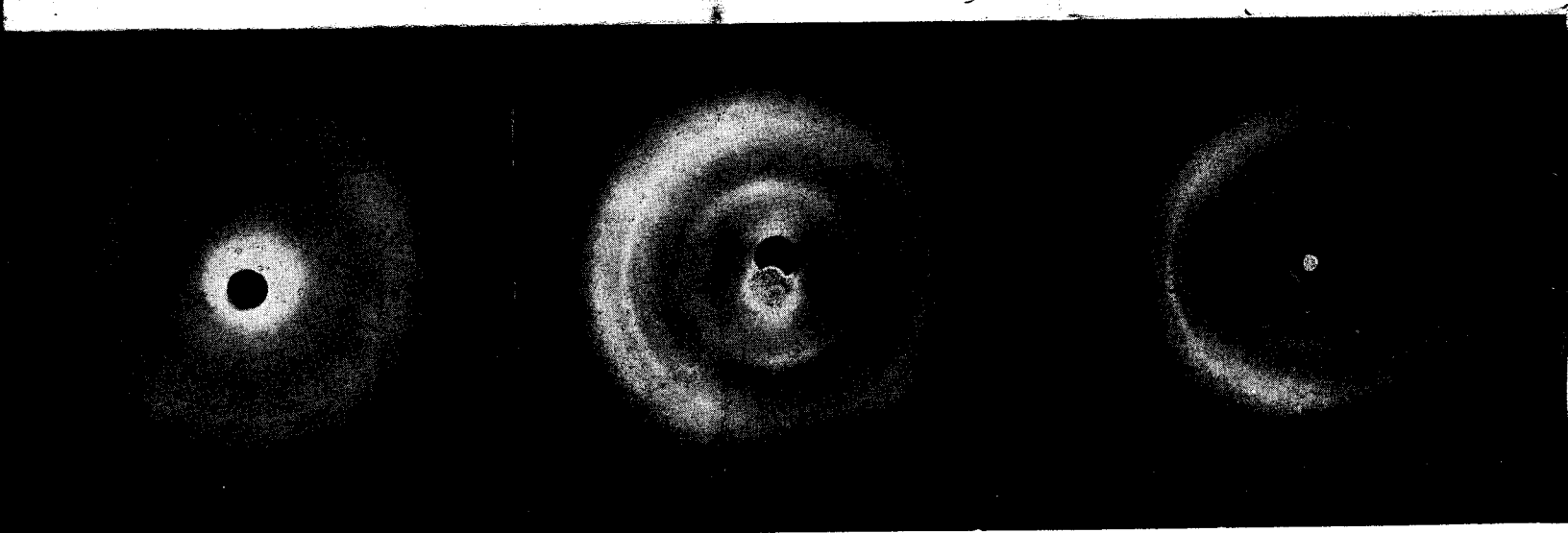
P. III.
W. M. Cordite
Accelerated ageing
70°C (80 hrs.)



P. IV.
W. M. Cordite
Cooled to liquid air tempt.
(5 hrs)

P. V.
W. M. Cordite
Liquid air treated sample
subjected to accelerated
ageing 70°C (80 hrs.)

P. VI.
A. N. Cordite
Fresh Sample (1953)



P. VII.
A. N. Cordite
After natural ageing
(10 yrs.)

P. VIII.
A. N. Cordite
Accelerated ageing
70°C (80 hrs.)

P. IX.
A. N. Cordit
Cooled to liquid air tempt.
(5 hrs.)