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NDRC 8 Monthly Report for November 1-30, 1942

Powder Pictures of Diamines and Triamines. A series of powder pictures of typical active and inactive chelates has been started. When completed these will be reported in the form of tables of spacings and relative intensities after the fashion of the Hanawalt Tables.

Oxidation Experiments. In the last report the question of equilibrium was mentioned. The following experiment is of interest in this connection. Two of the samples mentioned in that report were allowed to stand for three weeks in 9 cms. of pure oxygen at room temperature, which varied ±0.5° from 24°C. One was originally about 66% oxidation and the other about 54%. After one week they stood at about 68% and agreed with each other within experimental error. In the following two weeks their weights varied randomly within the limits of weighing errors. An x-ray sample was then extruded and photographed in 9 cms. of oxygen with one of the weighing bottles in the camera. The latter changed during the exposure by only 0.1 mg., less than the possible weighing error. The photograph is indistinguishable from the 66% picture made previously, at least within the limits of visual estimation. The presence of the strongest unique oxygen-free line is just detectable. The 66% sample was therefore presumably in equilibrium. This sample is in the percent oxidation range where the rate is fairly high and it is probable that for very low percent oxidations the equilibrium might be slower.

The oxidation studies are to be further checked with a fresh sample recently sent from Berkeley.

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Deteriorated Materials. A number of deteriorated materials have been photographed. Most of these are samples supplied by Professor Geissman at UCLA and are taken from larger batches sent him from Du Pont for analysis. The numbering of these samples is that used by Professor Geissman.

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A-2953. A check sample of the Rumford material used in preparing the later samples. Photographs of the oxide and the oxygen-free forms agree with previous pictures of Rumford salcomine.

A-2607. A sample ground for 20 hours in a ball mill while suspended in white oil (suspension 29% by weight) and then freed of oil. The activity has dropped to 3.7% uptake when deoxidized at 110°C and about 4.2% when deoxidized at 170°C, both deoxidations being at 25 mm. pressure of air.

The x-ray photograph of a sample deoxygenated in vacuum at 100°C is indistinguishable from that of A-2953 except for a few specks scattered over the film. These indicate the presence in the sample of a small quantity of coarse grained material. They fall in the proper places for rings of the inactive salcomine such as crystallizes from alcohol but the identification, although probably correct, is not very certain. The original material, in equilibrium with air, shows the same specks and moreover the ring system differs slightly from the oxide pattern of A-2953. The two extra lines which vary in intensity from preparation to preparation are here much stronger than on any photograph previously prepared. And there is also a weak line present which coincides exactly with the most intense unique line of the oxygen-free pattern. In this respect the picture looks very much like the 66% oxidation picture of the oxidation series reported last month. The quantity of oxygen-free material is however slightly greater. That this line really represents oxygen-free material is indicated by its behavior on exposing samples to oxygen. After the deoxygenated sample was exposed to air for several days and to one atmosphere of oxygen for 18 hours this line was very weak, almost absent. Upon exposing some fresh A-2607 to one atmosphere of oxygen for 100 hours the line also decreased in intensity but not as much as for the sample which had been

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first deoxygenated in vacuum at 100°C for one and one-half hours.

These results seem to indicate that the sample contains 10 to 15% of active oxygen-free salcomine which is prevented from absorbing oxygen, probably by some material forming a protective coating about the cyrstallites. The 100° C vacuum treatment seems to destroy some of the coatings. This sample differs from the 66% oxidation sample chiefly in that the oxide form is carrying a full quota of oxygen.

A-2595. A sample cycled 360 times in 180 hours while suspended in white oil, and then freed of oil. The activity was given roughly as 0.8 to 1.0% uptake or about 16 to 20% of the theoretical value. Professor Geissman reports orally that he is able to recover on hydrolysis about 80% of the theoretical original salicylaldehyde.

Pictures were made before and after deoxygenation in vacuum at 100°C. Both of these show spotty rings indicating the presence of a considerable quantity of coarse grained inactive salcomine, the modification obtained from alcohol. The identification is certain. The original A-2595 shows smooth rings of both the oxygenated and the oxygen-free active salcomine. The deoxygenated sample shows only the oxygen-free pattern. Because of conflicting rings from the inactive form it is difficult to estimate the relative quantities of the two forms present in A-2595. It seems certain however that there is more oxygen-free material than oxide in the sample when in equilibrium with air. No picture has yet been prepared of the material after reoxygenation, to see if more oxide will form after treatment in vacuum at 100°C.

The conclusion is that the deterioration is partly due to entrapment of oxygen-free crystallites in insulating coatings of some kind and partly due to

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conversion of the active to the inactive form. It is also probable that there is some destruction of salcomine completely but it will probably be impossible to detect or identify any decomposition products with such a complicated photograph, particularly as they are probably present only in small percentages. The principal constituent of the sample is inactive salcomine. If one ascribes the activity of about 18% to the oxide form observed, it must be present to the extent of 18%, the oxygen-free form is present in larger quantity, say 25%, and the inactive form would be present in sufficient quantity, namely about 35% to account for the salicylaldehyde recovery of about 80%. These are rather wild guesses. Professor Geissman has more recently recovered from A-2595 by benzene extraction a fraction of about 40% by weight which consists of red-brown needles which he says are inactive.

An x-ray pattern has been made of this material. It shows only the lines of the inactive salcomine which crystallizes from alcohol. No other substance can be present in very large quantities. The lines are spotty and indicate the crystallites may be as large as 10^{-2} cms. It is known that both active and inactive crystals may be obtained from benzene solutions so the rough agreement between the estimate above of 35% inactive material in A-2595 and the amount of this stuff recovered, 40%, cannot be considered very significant unless one believes that there is a fundamental difference in configuration between the molecules of the active and inactive forms and that the transformation from one to the other in solution is slow.

G-1. A sample deteriorated by repeated cycling dry in a tubular interchanger by Professor Gilliland at MIT. The details were not stated but the activity is said to be about the same as for A-2595. Three pictures have been prepared, one as received, one after deoxygenation for one and one-half hours in vacuum

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at 100°C and one after subsequent reoxygenation in one atmosphere of oxygen for 15 hours.

None of these show any traces of the inactive form, and they seem relatively weak in relation to the background, a fact which may indicate the presence of considerable amorphous material. All pictures, surprisingly enough, seem to be chiefly the oxygen-free pattern. The oxide lines appear very faintly for the original sample and much stronger on reoxygenation. If the sample supplied was in equilibrium with air it is difficult to account for the claimed activity because the pictures does not indicate the presence of 18% of the oxide.

The pictures seem to indicate that in part at least the deterioration is due to entrapment of active oxygen-free material in a coating of decomposition products.

General. It is not possible from the pictures made so far to estimate the grain size (except for coarse grained material). It is quite possible that some of the deteriorations are accompanied by decrease in particle size. In particular the G-1 pictures look as if this might be a factor. The results indicate that it should be possible to recover a considerable amount of salcomine from the deteriorated materials and that it might be possible to partially restore the activity of the samples by suitable treatments. One might try, for instance, heating in high vacuum at various temperatures and for various periods of time.

Pasadena, California
December 7, 1942

Signed Edward W. Hughes
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