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Deteriorated Samples. The following samples from Professor Geissman are identified by his numbering.

A67. Rumford salcomine after 1700 cycles at 80 psi with wet air in a packed reactor. Final capacity (Geissman) 0.1 to 0.2% uptake. MIT reports about 0.7%. Aldehyde recovery 60%.

The powder photograph shows a heavy background on which is superimposed the O-free pattern. No trace of the strongest unique oxide line is visible. After heating in vacuum at 100°C for two hours and treatment in one atmosphere of oxygen for 18 hours the oxide line is easily visible but still corresponds to a rather small percent of oxide. There is probably a lot of amorphous material and most of the salcomine is entrapped as O-free material.

R-1-32-I. The residue from A67 after benzene extraction. The photograph shows faint O-free lines but the material is largely amorphous.

A68. Rumford salcomine after 2050 cycles at 80 psi with dry air in a packed reactor. Final capacity (Geissman) 0.15 to 0.25% uptake. MIT reports about 1.3%. Aldehyde recovery 70%.

The powder photograph is in every way like that from A67 except that by both visual inspection and densitometry the ratio of the O-free lines to the background is greater. This indicates a smaller proportion of amorphous material. After heating in vacuum for two hours at 100°C and reoxidizing in one atmosphere of oxygen for twenty hours the strongest unique oxide line appears even more strongly than the corresponding O-free line. This indicates that considerably more than half of the material has been converted to the

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oxide. The rate appears very low however as after only a few hours in pure oxygen the line is still weaker than the O-free line. This sample is quite clearly less completely deteriorated than is A67.

It is unfortunate that such large discrepancies exist between the capacities measured for these samples at UCLA and at MIT. The x-ray pictures support the low values for the samples as received in equilibrium with air but support the higher values for prolonged oxygenation after heating. They are also in accord with the high aldehyde recovery, indicating that much of it comes from unchanged salcomine entrapped as the O-free form.

X-1. Salcomine made by the pyridinate method. This gives normal pictures in both the oxide and O-free forms. The "impurity" lines are quite faint.

R-1-35-I. Thimble residue from X-1 after benzene extraction amounting to 11% of the original. The x-ray pattern is that of coarse grained inactive red isomer. Since the pictures of X-1 show that X-1 cannot possibly have so much red isomer in it, if any at all, the large thimble residue must have been formed by recrystallization during the extraction.

Powder pictures of diamines and triamines. A complete set of pictures of all samples has now been made. All anhydrous and inactive materials were heated to 100°C in vacuum for one hour, cooled, and extruded for photographing in vacuum. All hydrates and active compounds which are not too fast were heated to 120°C in vacuum for one and one-half hours, cooled in nitrogen, extruded rapidly and photographed in vacuum. For the active diamines, oxygen was then admitted to the camera and an oxide picture started after one hour. For the very fast compounds (3-methoxy,3-ethoxy, and 3-fluoro-sal-en) oxides were extruded in air and photographed in air. After inserting fresh film the camera was evacuated and the sample temperature was raised to about 95°C for an hour.

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This was possible as this whole series of pictures was made in a camera subject to temperature control of the sample up to 100°C. The sample was then cooled to room temperature and the exposure of the O-free form was made in the vacuum which did not need to be broken after heating.

All these samples were photographed without any attempt at reducing the grain size to proper dimensions for good powder photographs. It seemed desirable to find out about the grain sizes for one thing and also we wanted a record of the pattern before grinding, even if a poor one, as a check against phase changes on grinding. As a result some of the pictures are so bad that new photographs will have to be prepared after grinding and sieving before good spacing measurements can be made. These coarse grained samples include 3-isopropyl-6-methyl-sal-en, 5-methoxy-sal-en, sal-N-methyl-pr-tr, 5-nitro-sal-pr-tr, 3-chloro-sal-pr-tr, 6-chloro-sal-pr-tr, 4-nitro-sal-pr-tr and 3-methoxy-sal-pr-tr. Even though some of these were hydrates they seem to have maintained particle size during dehydration. The compounds o-hydroxy-acetophenone-en and 3-nitro-sal-en show coarse structure on just a few lines, the rest being smooth. This probably indicates the presence of a coarse grained impurity in the sample.

On the other hand a few samples showed extremely fine grain size, so small that lines are not visible but only broad halos or diffuse background. The particle size in these cases must be at least less than 10^{-6} cms. They are the parent triamine itself, 4-hydroxy-sal-en, and 5-methyl-sal-pr-tr, all active. The parent triamine was supplied as a hydrate nicely crystalline with crystals large enough to be handled individually. During dehydration these turn from yellow to dark red but appear otherwise unchanged. The resulting crystals are pseudomorphs consisting of extremeley small crystallites.

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Some of the pictures show effects obviously due to preferred orientation of crystals in the samples. This usually occurs when the crystallites have very asymmetric shapes such as for extremely thin plates or fine needles. These effects occur for sal-N-methyl-pr-tr, 4-methoxy-sal-en, o-hydroxy-acetophenone-en, 3-chloro-sal-pr-tr and 3-methoxy-sal-pr-tr.

Pictures of both oxide and O-free forms were made only for the diamines. The oxygen pressures required for the triamines are in general too high. The three compounds 4-methoxy-sal-en, o-hydroxy-acetophenone-en and 3-nitro-sal-en show but minor differences for a few lines between oxide and O-free form and the accompanying color changes on oxidation, if any, were hardly noticeable except for the 3-nitro compound. The remaining active diamines, (3-methoxy, 3-ethoxy and 3-fluoro) show even greater differences between their oxide and O-free patterns than does the parent compound and they also show a pronounced color change on oxidation.

There is little similarity between the pictures of different compounds. The most striking resemblance is between 3-methyl-sal-en (inactive) and the O-free form of 3-methoxy-sal-en. Here the four most intense lines are almost the same in spacing and relative intensity. But weaker lines are quite different. There is no obvious relationship between the pictures of 3-methyl-sal-en and 3-fluoro-sal-en although the molecules, if of the same configuration, would be almost identical as to size and shape. Perhaps other modifications exist of one or both of these.

<u>Co-3-ethoxy-sal-en from various sources.</u> The 3-ethoxy-sal-en samples from the three sources, yellow hydrate, red hydrate, and pyridinate, yield pictures so nearly identical in both forms that at present it seems likely that the few small discrepancies seen are to be ascribed to differences in preferred orientation, particle size and possibly to small amounts of impurities.

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Although these samples yield good powder pictures which indicate particle sizes less than 10^{-3} cms, they are seen under the microscope to consist of rather large pseudomorphs after the parent solvates. Since the pseudomorphs from the two hydrates give fair extinction between crossed nicols and show pronounced dichroism, it seemed that the crystallites in the pseudomorphs must be rather well oriented. This has been investigated with the following results to date.

The red hydrate is monoclinic, occurring as thin parallelopipeds. The angles between the edges are about 78° and 102°. The b_o axis bisects the obtuse angle. They show symmetrical extinction and strong dichroism, being red with the electric vector parallel to b_o and yellow with it perpendicular thereto. Edgewise views are unobtainable under the microscope. After dehydration and oxidation the extinction is not perfect but is still good and is symmetrical. The pseudomorphs are dark yellow with the electric vector parallel to the former b_o axis of the hydrate and black with it perpendicular thereto.

The yellow hydrate is probably also monoclinic although this is not yet confirmed by x-ray pictures. It occurs as lath-like needles. When viewed normal to the lath face extinction is oblique, at about 40° from the needle axis. There are either impurities present or else some few individuals in which the laths are seen edgewise. These show parallel extinction. There are frequent twins in which the needle axis and b_o are common to the two individuals (b_o is normal to the lath face). These individuals extinguish one at 40° and the other at 50° to the needle axis. The dichroism is slight. They are very pale yellow with the electric vector in one extinction position and a darker yellow with it in the other extinction position. After dehydration and oxidation extinction is still quite good, and seems to be parallel. The dichroism is very curious. Some pseudomorphs are black with the electric vector

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parallel to the needle axis and red with it perpendicular thereto, but about as many others have the colors reversed.

Samples of the pyridinate are not at present available. The oxide from it shows pseudomorphs which do not change on rotation between crossed nicols and which are uniformly dark for all positions of the electric vector in polarized light.

Some red hydrate crystals have been examined by x-rays. The monoclinic symmetry has been confirmed and $a_0 = 13.75$ Å while $b_0 = 11.52$ Å. a_0 was chosen as the bisector of the acute angle of the parallelogram face. The remaining constants c_0 and β were not determined. One of these crystals while still mounted was heated to 120°C in vacuum for an hour and exposed to air. Although the mounting cement shifted it was possible to reorient the pseudomorph on a goniometer head as the faces still gave rough signals. One oscillation picture and several pictures without oscillation show that the crystallites are oriented quite well considering that this pseudomorph has undergone two transformations, a dehydration and an oxidation. The pictures are still being made and the interpretation will have to be carried out with some care as it is not certain that the crystallites tend to be oriented in only one direction nor is the symmetry of the crystallites yet known. But this line of attack seems to offer some promise of finally indexing the powder photograph.

Corresponding pictures of the yellow hydrate have not yet been made as all crystals so far examined that are large enough have proved to be twins.

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It need hardly be pointed out that the differences in rates observed at Berkeley for the materials from the different sources are probably related to the differences in size and orientation of the crystallites in the pseudomorphs.

Pasadena, California
February 6, 1943

Signed Edward W. Hughes
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copies 2-Calvin
1-Pauling
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Approved Linus Pauling
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