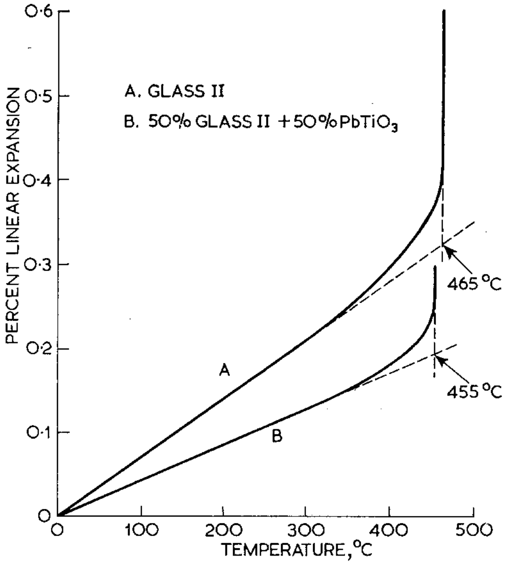

Figure 2 Transition temperature of Glass II as affected by internal stresses in Glass II-PbTiO$_3$ composites.

glasses were annealed. The stresses calculated from these shifts in transition temperature are 6300 psi for Glass I composites and 4600 psi for Glass II composites.

TABLE II Some Second order properties of glass I and glass II

Property	Glass I	Glass II
Transition temperature, ° C	473	465
Specific volume, cc gm^{-1}	0.42	0.25
Difference in volumetric expansion coefficient, ° C^{-1}	1.2×10^{-4}	1.8×10^{-4}
Difference in specific heat, cal gm^{-1} ° C^{-1}	0.03	0.028
dT/dp, ° C kbar^{-1}	31.0	29.5

It may appear at the outset that the stresses calculated from the changes in the transition temperature of glasses are considerably lower than expected. These are, in fact, very high and can be explained as follows: stresses in glass-crystal composites are developed due to the difference in expansion of the components as the composites are cooled from the hot-pressing temperature to room temperature. The magnitude of this stress (as can be calculated from the equations given in the literature [5, 6] is proportional to: (i) the cooling range, and (ii) the difference in expansion between the two components. To measure the transition temperature of glasses in glass-crystal composites, the composites are heated past the transition point to the softening point, where, again, no stresses exist. The stresses are maximum at room temperature; and, as the composites are heated, the stresses are lowered. In other words, only the stresses corresponding to the temperature difference between the transition point and the so-called upper no-strain temperature of glass can influence the transition temperature. The changes in the transition temperature of glasses are not reproducible from one run to the next on the same sample. This fact can be attributed to viscosity-time-temperature relations, since it is known that the residual stresses in glasses held at the transition temperature can be relieved with time.

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R. R. TUMMALA
A. L. FRIEDBERG
IBM, East Fishkill Facility
New York
USA

Temperature-Dependence of Characteristic Properties of α-Fe$_2$O$_3$ Powders

It has been shown in [1] that the "activity" of ferric oxide prepared by decomposition of various iron salts depends on the initial salts employed. Properties of ferric oxide also depend [2, 3] on its heat-treatment.

The aim of this note is to present the analysis (specific surface area, particle size and shape, particle size distribution and catalytic activity measurements) of α-Fe$_2$O$_3$ powders prepared by thermal decomposition of four hydrated iron salts (as in [1]) and calcined to different temperatures – 700, 900 and 1100° C.

The initial salts (hydrated ferrous sulphate, Mohr's salt, hydrated ferrous oxalate and basic iron carbonate) were heated in air in a furnace at 650° C for 10 h; the temperature was then raised to 700, 900 or 1100° C and the samples were kept in the furnace for another 2 h at their respective temperatures. The furnace with the samples was cooled at 1° C min^{-1}. Chemical analysis did not reveal traces of anions in any sample. X-ray patterns exhibited the hexagonal modification of α-Fe_2O_3. Weight difference of the studied samples and samples heated 2 h at 1150° C were less than 0.05%. Specific surface area was measured by the method described in [4].

Photomicrographs were obtained on a Zeiss (Jena) optical microscope. The particle size distribution was studied by a sedimentation technique [5]. The catalytic activity was measured by the model reaction of decomposition of methylalcohol in a pulse-type apparatus operating in a chromatographic regime [6]. X-ray patterns were provided with a diffractometer URS-50 IM (USSR) using FeKα radiation. The colour of samples in reflected daylight measured by means of a spectrophotometer SF-20 (USSR) is described in [7].

In the following text the ferric oxide samples are designated according to table I.

TABLE I Designation of ferric oxide samples

Initial iron salt	Heat-treatment at ° C		
	700	900	1100
Sulphate	No. 6	No. 16	No. 26
Mohr's salt	7	17	27
Oxalate	8	18	28
Basic carbonate	9	19	29

As shown in fig. 1 the samples treated at 700° C have the greatest specific surface area of all the ferric oxide powders; values m^2 g^{-1}) for individual samples are: No. 6 = 9.0, No. 7 = 12.6, No. 8 = 1.8 and No. 9 = 5.9. The substantial differences between these values are caused by the fact that with samples Nos 6 and 7 the temperature of 700° C is practically identical with the decomposition temperature of the initial salt, while with samples Nos. 8 and 9 it is substantially higher than the decomposition temperature. Variation of both specific surface area and particle size in relationship to the treatment temperature from 700 to 1100° C is the greatest with samples obtained from Mohr's salt: the surface area of sample No. 7 is 75 times greater than with the sample No. 27.

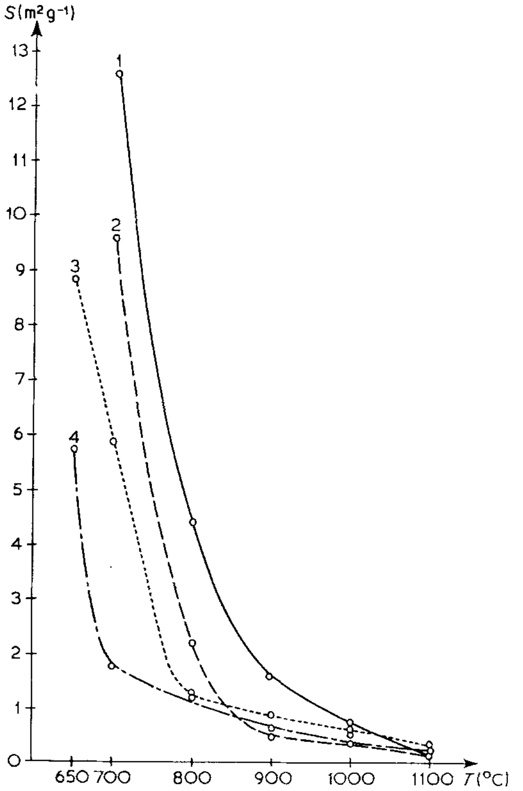

Figure 1 Dependence of specific surface area (*S*) of ferric oxide on the sort of initial iron salt and its temperature treatment. Initial salts used: Mohr's salt (curve 1), ferrous sulphate (curve 2), ferrous oxalate hydrated (curve 3) and basic iron carbonate (curve 4).

The photomicrographs in fig. 2 indicate that samples Nos. 7 and 9 consist of particles mostly homogeneous in size (0.5 to 7 μm and 7.0 to 15 μm respectively). The size of conglomerates in sample No. 6 varies from 0.5 to 30.0 μm, in the sample No. 8 from 0.8 to 35 μm. The particle size increases with the rising temperature of treatment, conglomerates formed being more spherical in shape and losing the originally irregular shape. With the samples treated at 1100° C the dimensional non-homogeneity of particles in all samples is regularised at a mean value of 5 to 60 μm.

It also follows from fig. 2 and table II that the grain growth process is most intensive in samples obtained from ferrous sulphate and Mohr's salt, while in samples obtained from ferrous oxalate small particles do not disappear even after heat-treatment at 1100° C. The ratio of the mean surface area diameters of particles calcined at 1100° C and those calcined at 700° C are: 3.2 for

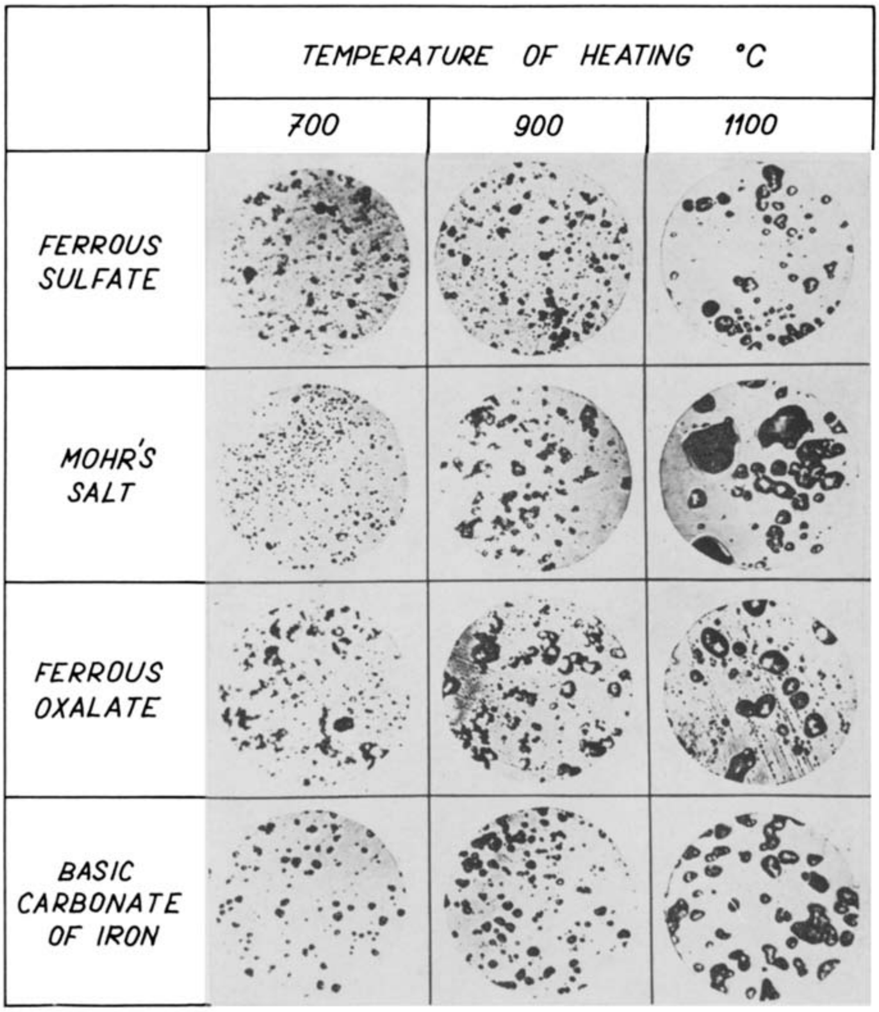

Figure 2 Photomicrographs of ferric oxide particles formed from various salts with differing thermal treatments (×150)

ferric oxide prepared from Mohr's salt, 3.1 for sulphate-derived oxide and 1.5 and 1.9 for oxalate- and carbonate-derived oxides, respectively.

Results of sedimentation analysis [5] in fig. 3 show that with increasing treatment temperature the content of fine particles in the samples decreases and the size of the largest particles rises to 70 μm. As follows from table II it is necessary to take into account the aggregation of crystallites. The degree of aggregation (which is the ratio of mean particle diameter, evaluated from sedimentation analysis (fig. 3), to that evaluated from surface area measured), depends on the initial iron salt and its thermal treatment. The greatest degree of aggregation is generally found with samples calcined to 700° C and decreases with the rising treatment temperature. Ferric oxide derived from Mohr's salt exhibits a considerable degree of aggregation, while oxalate derived oxide shows the lowest one. Samples treated at 1100° C indicate a similar degree of aggregation and also similar surface area (0.1 to 0.2 m^2 g^{-1}).

As both the grain growth and the aggregation processes are closely related to the "activity" of the material [8], the present results confirm previous conclusion [1] of considerable deactivation of oxalate-derived ferric oxide even at 700° C, while sulphate or carbonate-derived oxides maintain a relatively higher degree of "activity" up to this temperature.

TABLE II Characteristic of ferric oxide particles with different chemical origins and thermal treatments. Designation of samples after Table I.

	Designation of Fe_2O_3 powder											
	6	16	26	7	17	27	8	18	28	9	19	29
Mean particle diameter from sedimentation analysis (μm)	4.15	6.17	12.9	4.29	8.60	12.8	6.50	8.30	10.2	5.85	6.70	11.2
Mean particle diameter from surface area measurement (μm)	0.13	2.43	7.50	0.10	0.70	7.50	0.67	1.90	6.30	0.20	1.33	4.00
Degree of * aggregation	32.0	2.5	1.7	42.9	12.3	1.8	9.7	4.4	1.6	29.3	5.1	2.8

*Degree of aggregation = mean particle diameter from sedimentation analysis: mean particle from diameter surface area measurement.

Similar results concerning particle size and solubility of ferric oxide were published by Hedvall [9]. The solubility of different samples in 1 m H_2SO_4 decreases with their treatment temperature: the greatest difference of solubility between samples treated at 700 and 1000° C was observed with ferric oxide prepared from Mohr's salt, the smallest with oxalate-derived oxide.

The catalytic activity (CA) of α-Fe_2O_3 powders is expressed in per cent of methylalcohol conversion related to 0.1 g of the catalyst. Fig. 4 shows catalytic activity values of ferric oxide at 530° C based on the model reaction of methylalcohol decomposition in dependence on the procedure and temperature of preparation of the catalyst.

The highest catalytic activity is observed with samples prepared at 700° C, i.e. the lowest

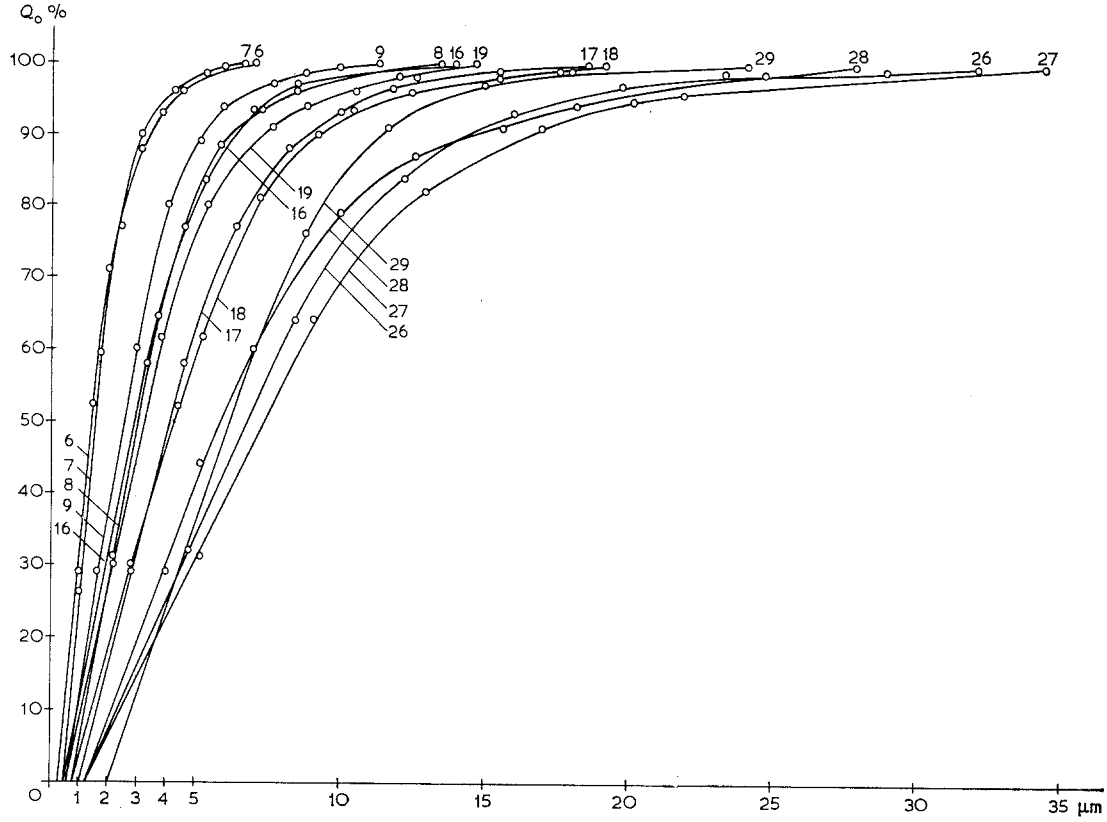

Figure 3 Particle size distribution of ferric oxide with various chemical origins and thermal treatments. The designation of ferric oxide samples is given in table I.

temperature used in our experiments for heat-treatment. At this temperature samples are deactivated to a high degree (the highest value is CA = 40%), deactivation being most visible with oxalate- and carbonate-derived samples. The activity of the catalyst decreases with its treatment temperature and all samples prepared at 1100° C have a very low CA-value (2 to 5%).

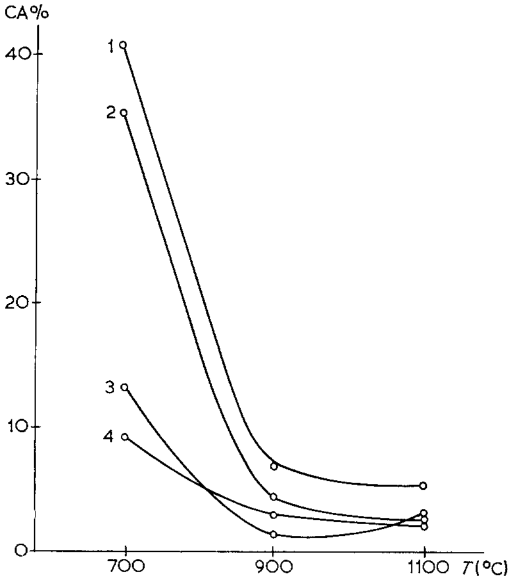

Figure 4 Dependence of the catalytic activity (CA) of ferric oxide on the sort of initial iron salt and the temperature of its treatment.

The results presented, of the temperature-dependence of characteristic properties of α-Fe_2O_3 powders are in excellent agreement with a study of Fe_2O_3—sintering [10].

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V. BALEK
Department of Radiochemistry
Charles University, Prague
Czechoslovakia