UNCONVENTIONAL METHODS OF OBTAINING CERAMIC PIGMENTS FROM GELS

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SUMMARY

The technology used for obtaining ceramic pigments has developed very little in comparison with that of other sectors in the world of ceramics manufacturing. The present work highlights some of the problems which affect the traditional method of synthesis of ceramic pigments, alternative methods of synthesis are proposed which are based on sol-gel methodologies and some results of interest obtained in turquoise and vanadium-zircon green, uvarovite victoria green and zircon-vanadium yellow.

Ceramic pigments are still made at present with methods which differ little from the traditional methodology. Although the development of new chromophore-host crystalline structures, such as that of zircon which makes available to the ceramicist the entire pallet of colours (1), cannot be considered to have been entirely exhausted, neither does it appear at present to be a promising line of research in the medium term within the field of ceramic pigments. It would appear that at present research in the field of ceramic colorants must place emphasis on the development of processing methods and batch systems which allow ceramic pigments to be obtained with criteria of optimization from both the economic and ecological points of view. **Amongst the problems which present-day traditional processing involves for ceramic pigments, the following may be emphasized:**

A. High energy costs owing to the high temperatures and long retention times necessary in the calcination of ceramic cakes.

B. Compositions complicated by the use of complex mineralizer systems which increase the cost of initial raw materials.

C. Contamination of the surrounding atmosphere and of waste water by elimination of mineralizers by chimney and by washing of calcinated products respectively (7).

D. Problems of homogeneity in the pigmenting power of the various batches of colour.

Most of the problems mentioned above have their roots in kinetic aspects of the synthesis of the pigmenting structure; both the use of mineralizers and the raising of temperature and retention times in calcination are necessary in order to achieve an acceptable hourly output of reaction synthesis; the degree of advance achieved in this process shall determine not only the shade but also the performance of the colour within the glazes.

How can the kinetics of the synthesis process be improved by non-traditional methods such as the addition of mineralizers or raising temperatures and retention times? While in solid-state reactions such as those which give rise to pigmenting structures a decisive factor in their kinetics is the microstructural factor, in the classic method the microstructure of the batch composition is limited by two basic factors: the particle size possible with mechanical grinding never being lower than 2 μ and the degree of homogeneity of the raw mixtures with scales always higher than 2 μ. Achieving starting batch microstructures of high homogeneity and low particle size is fundamental to the objective of achieving optimization of ceramic pigment synthesis. Sol- gel processes may provide an answer to these question marks by permitting interesting improvements in the microstructural factors with respect to traditional ceramic methodology.

The sol-gel method has been applied for many years now for obtaining inorganic oxides. As Segal (2) recounts, the sol-gel method met with its first widespread recognition by resolving the health problems faced by operators in nuclear power stations in handling the fine radioactive dust used in manufacture of the pills of nuclear fuel based on UO^2 oxide containing between 2 and 5% of U^{235} obtained by a conventional ceramic process. These problems were eliminated thanks to a sol-gel method providing the possibility of obtaining the oxide in the form of spheres which could be packaged using a vibration compaction method (2). The method was later used in those cases in which control of the purity, density and porosity of the oxides (such as catalytic bases) is necessary in order to deposit fine layers of oxide (from 0.1 to 2 μm) on a substratum, for immersion of the latter in a colloidal suspension of the oxide and subsequent calcination at temperatures of the order of 800°C or to increase the corrosion resistance of wire meshes of certain metal alloys such as the steel alloy known as Fecralloy, passivated by a layer of Al_2O_3 obtained from an alumina-sol and used as a catalytic platinum base in hydrocarbon oxidation processes (2).

The sol-gel method is widely used at present in the development of high-temperature glazes.

Such is the case with glazes of composition $3Al_2O_3.2SiO_2$ in which use of the gel method does not permit detection of the mullite crystallization until a temperature of 1.200°C has been reached, achieving total crystallization at no less than 1.400°C, while for normal glazes it does so from 1.000°C; another example cited by B.J.J. Zelinski (3) are Na_2O- ZrO_2-SiO_2 with high zirconium oxides contents.

The principle upon which these applications of the sol-gel method is based is briefly as follows.

We consider a system of α phases which by reaction in solid state achieve a system of phases.

With the traditional or ceramic method, managing to achieve the state of system equilibrium is limited by two basic factors:

1.- The ease of nucleation of the new phase associated with the free reaction energy $\Delta G<0$ of process (proportional to r^3, where r is the radius of the nucleus) to $\Delta G>0$ linked to the process of formation of a new surface (proportional to r^2), and to $\Delta G>0$ associated with the elastic stress involved in deformation of the network in order to accommodate the nucleus (proportional to r). Up to critical value of r, these last two components predominate and the nucleation is not effective; this critical value falls as does particle size by increasing the specific surface area between the grains where the formation of the new phase eliminates the interphase energy $\alpha - \alpha$.

2.- The speed of diffusion of the ions to make the nucleus formed by the new phase grows, clearly associated with the degree of homogeneity of the mix. As a consequence, nucleation and growth of the new phase are limited by the degree of homogeneity of the mix at microstructural level, which in the case of ceramic grinding never exceeds 2 μm In the sol-gel method, preparation of the samples follows the following phases:

a) the starting materials (colloids alone or together with soluble salts) disperse in acid medium in order to generate a colloidal dissolution. When operating from the starting point of alkoxides, the starting materials are dissolved in alcohols by adding the amount of water dispensed for hydrolysis of the system and the possible acid catalyser, the dissolution thus obtained being maintained by kept under backflow and constant shaking.

b) the addition of alkalis to the colloidal dissolution reversibly gellifies the system. In the case of alkoxides, the gel is produced by a hydrolysis- condensation process leading to a polymeric gel.

c) the gels obtained are dried slowly under an infrared lamp and calcinated at a temperature suitable for obtaining the material of interest.

The gels thus obtained are highly homogeneous amorphous solids (with scales from 10 to 100 Å), with the cations in environments of maximum coordination compared to any other amorphous phase (4). This high initial homogeneity means that the state of system equilibrium is achieved more rapidly and at lower temperatures. The fact that on many occasions this is not apparently so is due to the fact that from a thermodynamic point of view the gels obtained are systems of high free energy compared to that of the crystalline system in equilibrium and greater than the energy corresponding to the glass phase of the system, with sintering kinetics favoured by the small particle size in the gels (4). Thus, in transformation of the dry gel crystalline phase in stable equilibrium, glazes can and are obtained at temperatures lower than those of generation of liquid phase for a given composition.

In the field of ceramic pigments, the utilization of sol-gel methods has as its objective the development of gels which do not generate glass phases and are not unstable, allowing synthesis of the ceramic pigment at low temperature and with degrees of reaction close to those of equilibrium, which increase the chromatic performance of the pigment.

This has been in the pigment known as vanadium-zircon blue (5), obtaining colour performance from gels in the ZrO_2-V_2O_5-SiO_2 ternary system comparable to that of commercial pigment prepared by addition of a complex mineralizer system which includes NaF, and very much greater than that obtained by the traditional method, as can be observed by comparing the levels of reflectivity of the UV-V spectral curves of each of them glazed with a gloss lead glaze with 3% doses of the pigment with those of the reference control (Fig. 1). This pigment also shows colour development at lower temperatures with the use of the sol-gel methods (750°C, compared to the 850°C of the ceramic methods with or without NaF mineralizer, with retention times of 8 hours). Similarly for uvarovite victoria green (6), the sol-gel methods develop the uvarovite and the colour at lower temperatures (700°C compared to the 1.000°C of the ceramic methods, with retention times of 12 hours), giving a lighter and more pleasant green by reducing the unreacted free Cr_2O_3 content in the system. Other systems in which satisfactory results appear to be achieved are zirconium yellow and in non-colorant compositions of V_2O_5- P_2O_5-Al_2O_3. The electric microscope (Figs. 2, 3 and 4) reveals various results from a microstructural point of view, according to the system tested; in some cases the use of the sol-gel method provides highly sintered and crystalline materials compared to ceramic methods (zircon), while for others it gives crystalline materials of low particle size (aluminium phosphate with traces of vanadium).

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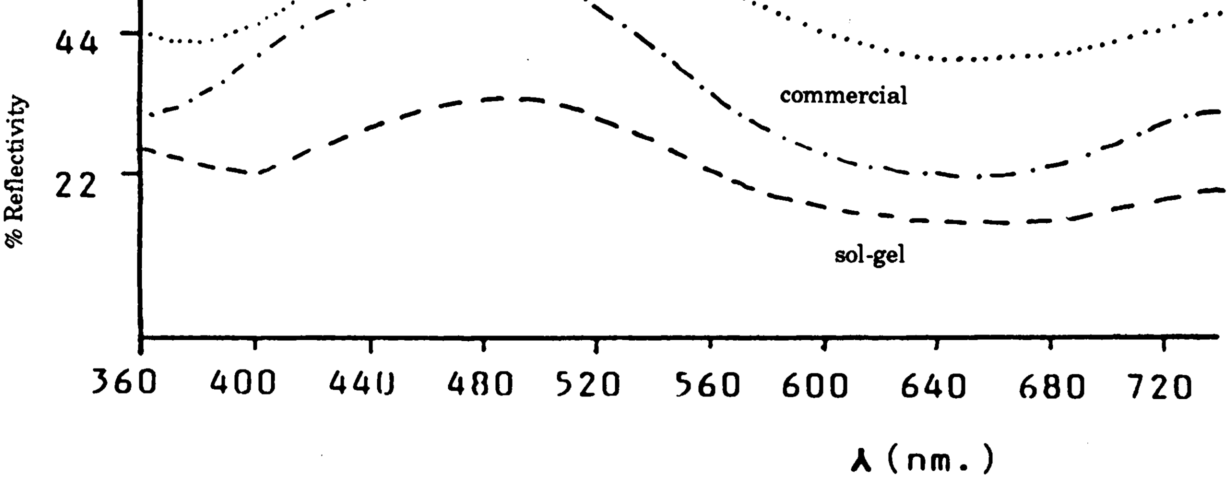
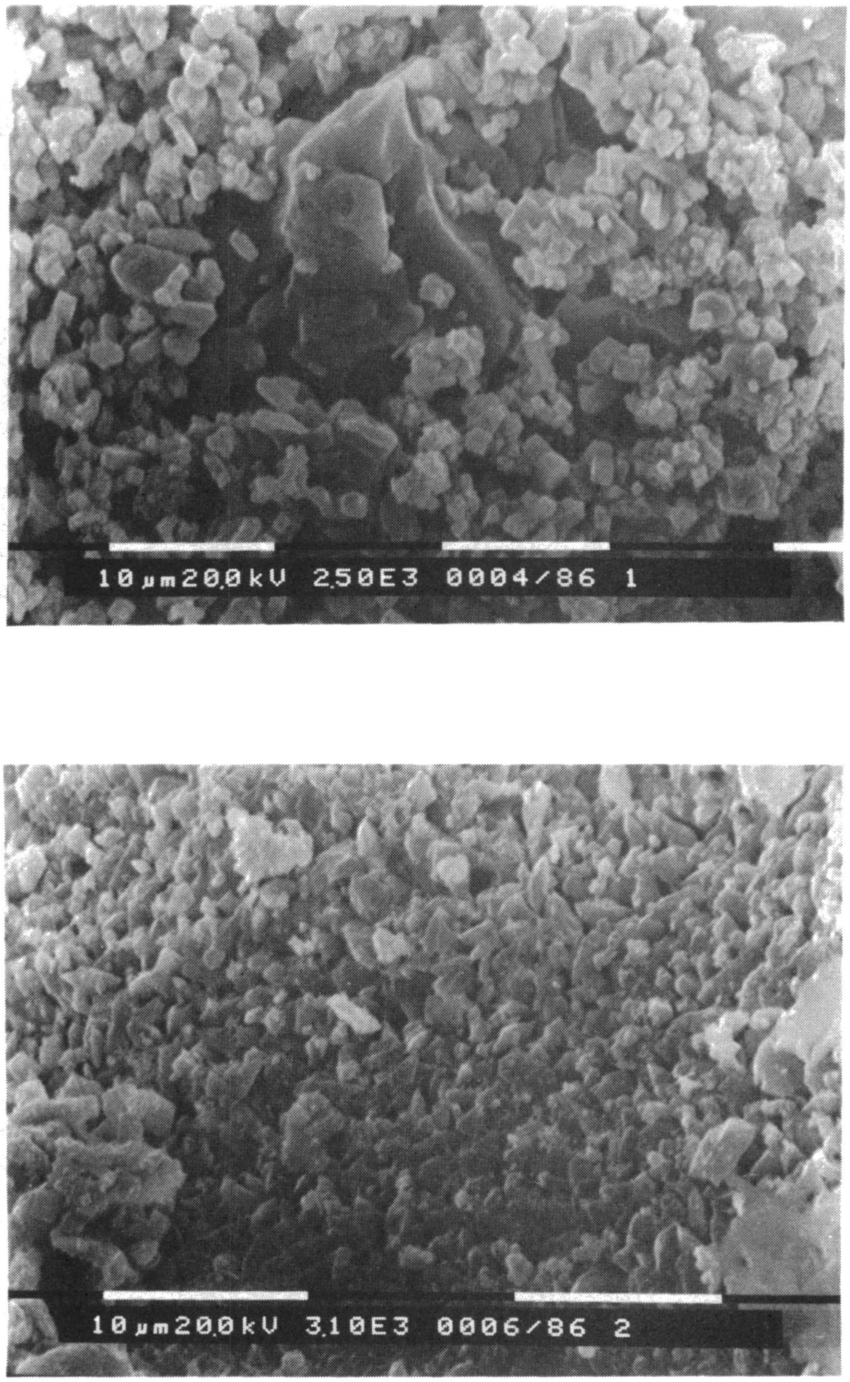
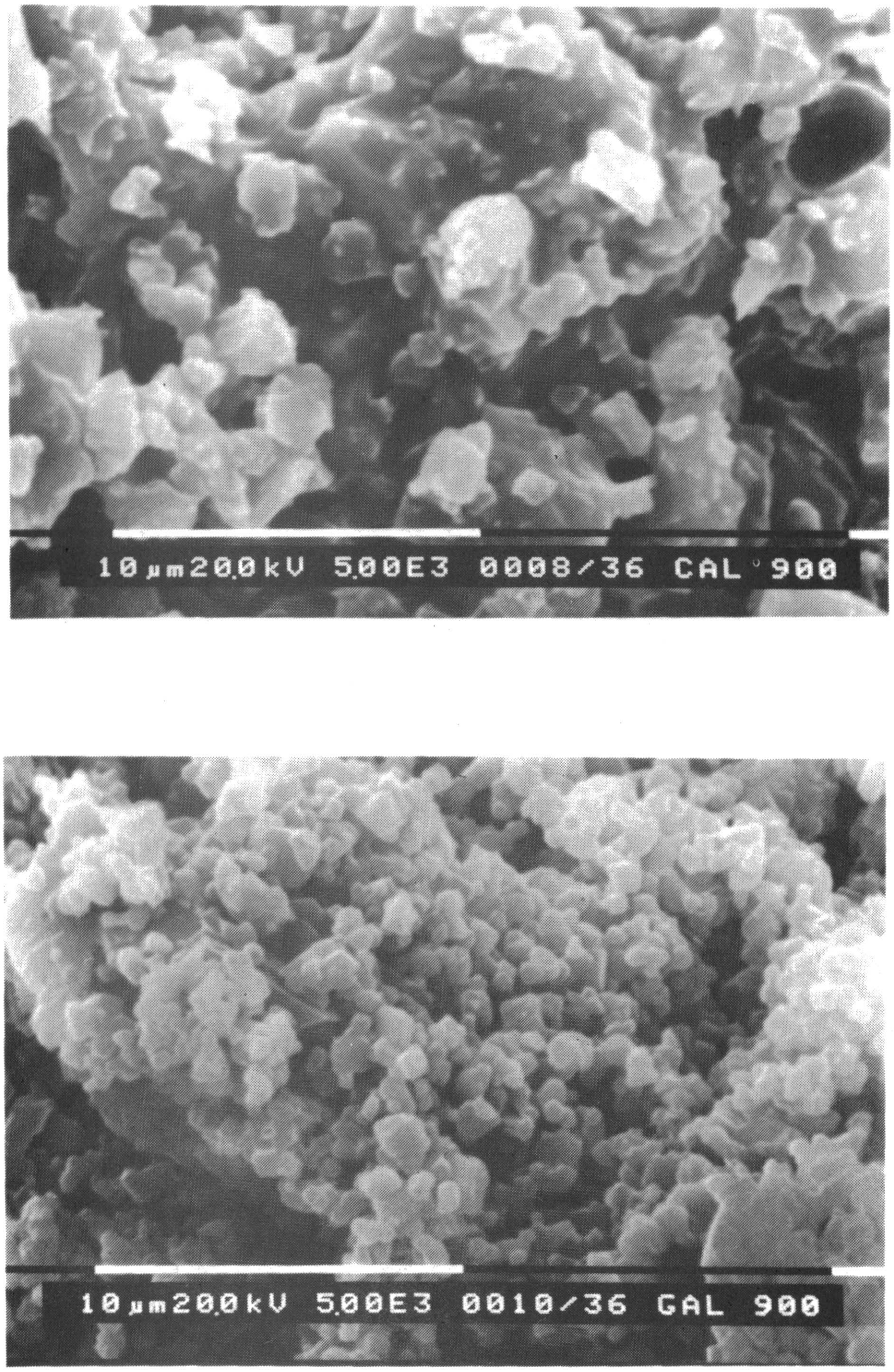
FIG. 1



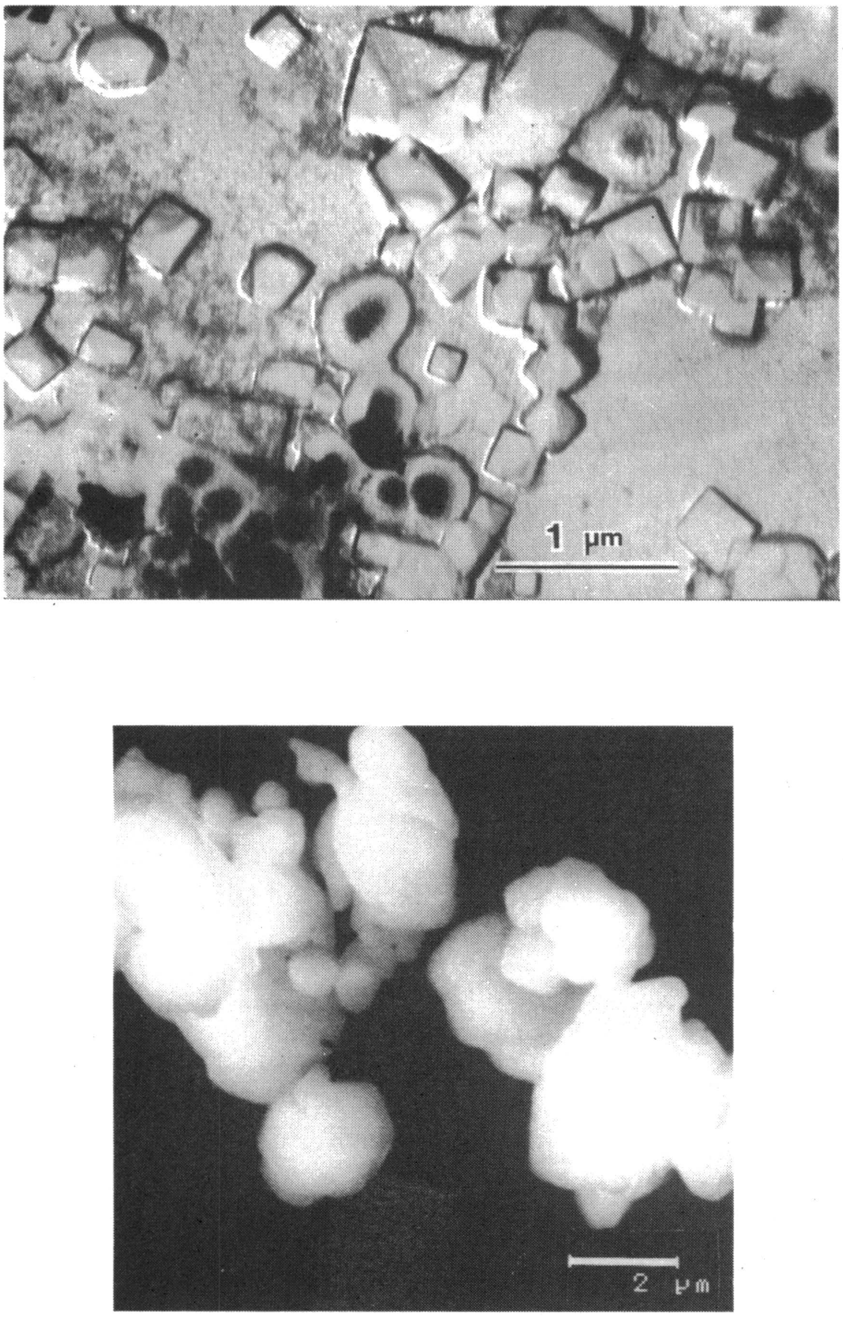
1.- Spectral curves for glazed plaques with 3% pigment in a bright lead-based transparent glaze.



2.- Microphotographs of zircon obtained by the ceramic method (800ºC/ 8h) (1) and of the one obtained by using a gel of silicon tetraoxide, zircon oscichloride and ammonium metavanadium (800ºC / 8h) (2). A division 10 um.



3.- Microphotographs of cristals of aluminium fosfate mixed with vanadium (V-A1PO 4) obtained by the traditional ceramic method (AL), with both samples being burnt at 900ºC/12h. A division 10um.



4.- Microphotographs of Verde Victoria de Uvarovita obtained by burning a gel of silicon tetraoxide chromium chloride (III) and calcium chloride at 1.000 ºC /12h.

Fig.4-A using a sweep microscope.

Fig.4-B using the replica technique with a transmission microscope.