

Combustion synthesis of cobalt pigments: Blue and pink

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Idiochromatic blue cobalt aluminate (CoAl₂O₄) and purple pyroborate Co₂B₂O₅ were prepared by solution combustion method using corresponding metal nitrates, boric acid and carbohydrazide mixtures. Allochromatic Co²⁺ doped in Al₂O₃/ZnAl₂O₄ and Mg₂B₂O₅ pigments having the same colour intensity as idiochromatic pigments were obtained similarly. All the pigments are voluminous, homogeneously coloured with a large surface area. The products are characterized by their characteristic colours, XRD, IR and electronic spectra.

CERAMIC pigments are important in the industry due to their applications in tableware, sanitaryware, tiles and glasses. They can be classified into two broad categories: a) idiochromatic and b) allochromatic pigments. Idiochromatic (self-coloured) pigments are those in which transition metal ions are an essential part of the structure and contribute to the nature of the ligand field. Chrome green Cr₂O₃ and Thénard's blue CoAl₂O₄ are some typical examples¹. Allochromatic (other coloured) pigments can be further sub-divided into two groups: a) substitution and b) inclusion type pigments. In substitution pigments, transition or lanthanide metal ions are present in the ligand field of the host lattice. For example, the pink colour of ruby (Cr³⁺/Al₂O₃) is due to trace amounts of chromium present in the octahedral site of the corundum lattice. Inclusion pigments are those in which coloured oxides are trapped or encapsulated in inert oxide hosts and can be considered as solid in solid type emulsion. The well-known red zircon (Fe³⁺:ZrSiO₄) pigment is red due to the entrapment of Fe³⁺ ion within a zircon crystal.

The important physical–optical properties of pigments are their light absorption and scattering properties that depend upon the wavelength, particle size, particle shape and refractive index. Thus, for coloured pigments, the optimum particle size should be 1–10 μm and they should possess high refractive index to give good tinctorial strength (ability of a colourant to impart colour)². Oxide materials like alumina, aluminates, silicates, borates, zirconia and zircons doped with transition metal or rare earth ions meet these requirements of ceramic colourants. Of these, the cobalt pigments are of paramount importance in ceramic industry due to their spectacular variety of colours, high tinting strength and remarkable stability under chemical, thermal and reducing conditions³.

The co-ordination chemistry of cobalt complexes has fas-

inated chemists since Werner's times due to the spectacular range of colours they produce. The various colours that these complexes are known to exhibit in solution are summarized in Table 1 (refs 4–6). It is interesting to note that the colours of cobalt (II) compounds are stereochemically specific depending upon the co-ordination site and number. While the octahedral cobalt compounds are generally pink to violet, the tetrahedral ones are blue. The production of different colours by cobalt compounds and ions is also possible in the solid state. Colours range from blue, green to pink depending upon the host lattice and co-ordination geometry. The conventional method for the preparation of these pigments is by the solid state reaction (ceramic method) using corresponding metal salts like oxides, carbonates, etc.⁷ This requires high temperature (1000–1400°C) and long processing time (several hours to days). The end products are usually coarse and inhomogeneous which render them inapplicable. They require further processing like wet or dry milling to produce fine powders. Addition of mineralizers is often necessary to facilitate the reaction in the fluid state.

The aim of this investigation is to prepare Co²⁺-based ceramic pigments by the solution combustion method. This method has been used successfully for the preparation of fine oxide materials⁸. We intend to obtain the blue and pink colours of idiochromatic pigments such as CoAl₂O₄ and Co₂B₂O₅ by doping minimum amount of Co²⁺ in Al₂O₃/ZnAl₂O₄ and Mg₂B₂O₅ in order to make the process economical.

The combustible redox mixtures contain metal nitrates as oxidizers and carbohydrazide (CH)/urea as the fuel for the synthesis of ceramic pigments. A stoichiometric calculation of the redox mixtures is to be made to ensure complete combustion without any carbon residue⁹. The Pyrex glass vessel containing aqueous solution of stoichiometric amounts of metal nitrates and fuel when introduced into a preheated muffle furnace (350°C–500°C) boils, froths, undergoes dehydration, ignites and burns to yield voluminous, foamy, homogeneously coloured pigments.

The spinel, cobalt aluminate (CoAl₂O₄) was obtained by

Table 1. Various colours of Co(II) complexes

Coordination compounds of cobalt (II)	Colour	Cobalt(II) coordination site
[Co(H ₂ O) ₆] ²⁺	Pink	Octahedral
[Co(NH ₃) ₅ Cl] ²⁺	Pink	Octahedral
[CoCl(H ₂ O) ₅] ⁺	Raspberry red	Octahedral
Co(CH ₃ COO) ₂ ·4H ₂ O	Violet red	Octahedral
[Co(bipy) ₃] ²⁺	Red	Octahedral
CoF ₂	Pink	Octahedral
CoCl ₂	Sky blue	Octahedral
[CoCl ₄] ²⁻	Blue	Tetrahedral
[Co(NCS) ₄] ²⁻	Blue	Tetrahedral
[Co(N ₃) ₄] ²⁻	Blue	Tetrahedral
[(C ₂ H ₅ O) ₂ PS]Co(C ₂ H ₅ OH) ₂	Blue	Tetrahedral
[Co(CN) ₅] ³⁻	Dark green	Tetragonal pyramida

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the combustion of an aqueous solution containing 10 g $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 3.9 g $\text{Co}(\text{NO}_3)_2$, and 4.5 g CH. The solution, when rapidly heated at 350°C undergoes smoldering type combustion with intermittent sparks and flame (flame temperature $\sim 1000^\circ\text{C}$) to give indigo-coloured pigment. The combustion yield is 13% giving 2.35 g of foamy cobalt aluminate (foam density = 0.015 g/cm^3).

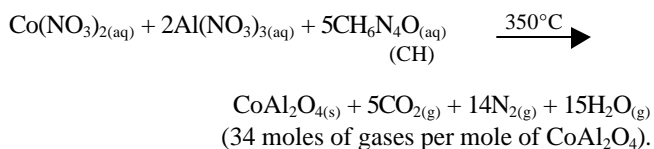
Cobalt doped zinc aluminate ($\text{Co}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$, $x = 0.03$) was prepared by the combustion of an aqueous solution containing 15 g $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 0.18 g $\text{Co}(\text{NO}_3)_2$, 1.6 g $\text{Zn}(\text{NO}_3)_2$ and 8 g urea. This solution was heated rapidly at 500°C . It undergoes flaming type combustion (flame temperature $\sim 1350^\circ\text{C}$) yielding 4.8 g (12%) of foamy blue coloured cobalt doped zinc aluminate (foam density = 0.017 g/cm^3). Similarly blue alumina (2.5 atom % of Co doping) was synthesized by rapidly heating aqueous solution containing 19.5 g $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 0.2 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 8 g urea at 500°C . The solution burns with a flame (flame temperature $\sim 1500^\circ\text{C}$) yielding 10% (2.8 g) of foamy cobalt doped alumina (foam density = 0.009 g/cm^3). Doping different atom % of Co produced various shades of blue alumina.

Cobalt pyroborate $\text{Co}_2\text{B}_2\text{O}_5$ was prepared by rapidly heating (at 350°C) an aqueous solution containing 5 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 1 g H_3BO_3 and 2 g CH. The solution undergoes smoldering type combustion (flame temperature $\sim 1000^\circ\text{C}$) to give a mauve pink (purple) product. The combustion yield is 24% giving 1.8 g of cobalt borate (foam density = 0.015 g/cm^3). Rosy cobalt pigment was obtained by heating an aqueous solution containing 20 g $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 1 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 4.8 g H_3BO_3 and 7.8 g CH rapidly at 350°C . The combustion is flaming type (flame temperature $\sim 1250^\circ\text{C}$) yielding 17% (2.9 g) of rose pink $\text{Mg}_2\text{B}_2\text{O}_5$ (foam density = 0.015 g/cm^3). In all these cases the system is self-propagating going to the transient high flame temperature (1000°C – 1500°C). The reaction occurs within 10 sec with no damage to the pyrex glass vessel.

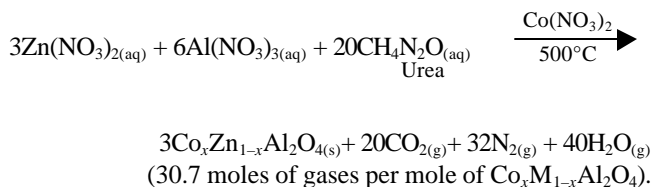
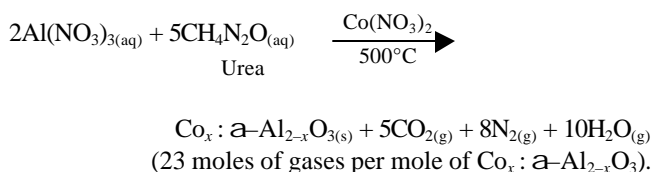
Combustion synthesized powders were characterized by X-ray powder diffraction patterns using a Shimadzu D-D1 X-ray diffractometer with $\text{CuK}\alpha$ radiation and nickel filter. Infrared spectra were recorded using a Bruker FTIR Multiscan 15sf II instrument in a KBr matrix. The UV-Vis spectra for the powder samples were recorded in a diffuse reflectance mode at room temperature with Pye Unicam SP8-100 UV/Vis spectrophotometer using MgO as reference. Kubelka Munk equation was used to change the reflectance scale to the absorbance scale. The powder density was measured using a pycnometer with xylene as the liquid medium. The 50 wt% average agglomerate size was determined by sedimentation and light scattering principle using Micron photosizer instrument (model SKC 2000). BET surface area of the powders was measured by nitrogen adsorption using Accusorb Micrometrics instrument (Model 2100E).

Both allochromatic ($\text{Co}_x\text{Al}_{2-x}\text{O}_3$ and $\text{Co}_x\text{M}_{1-x}\text{Al}_2\text{O}_4$) and idiochromatic (CoAl_2O_4) blue pigments were prepared as

described above and characterized by their colour, XRD and UV-vis spectra. The theoretical equations for the formation of CoAl_2O_4 assuming complete combustion may be written as follows:



The product is indigo in colour with a foamy texture (Figure 1). In a similar way, the equations for the formation of allochromatic blue pigments $\text{Co}_x\text{Al}_{2-x}\text{O}_3$ and $\text{Co}_x\text{M}_{1-x}\text{Al}_2\text{O}_4$ ($\text{M} = \text{Mg}$ and Zn , $x = 0.01$ to 0.2) can be represented as follows:



All the Co^{2+} (various proportions) doped $\text{Al}_2\text{O}_3/\text{ZnAl}_2\text{O}_4$ pigments are homogeneously blue in colour. The intensity of the blue colour gradually increases as the amount of Co^{2+} doping varies from 0.5 to 10 atom % in alumina as shown in Figure 2. At 5 atom % substitution the colour matches well to that of CoAl_2O_4 . Hence the optimum concentration of dopant (Co^{2+}) required to achieve the idiochromatic blue colour is between 5 and 7 atom % in alumina/ ZnAl_2O_4 (Figure 3).

The combustion synthesized pigments are all crystalline as reflected from their XRD patterns. Figure 4 shows the diffraction pattern of the spinel CoAl_2O_4 and Co^{2+} doped in various proportions in hexagonal $\alpha\text{-Al}_2\text{O}_3$ and the spinel ZnAl_2O_4 . The X-ray pattern of 0.5 atom % Co^{2+} in Al_2O_3 shows a single phase of $\alpha\text{-Al}_2\text{O}_3$. But as the substitution increases from 5 to 10 atom %, additional peaks start emerging. From 5 atom % onwards, CoAl_2O_4 phase starts appearing which becomes distinct at 10 atom %. The lattice parameters of the various blue aluminas refined with least square fit method show a gradual decrease in the 'a' and 'c' values when compared to the unsubstituted one. For a Co^{2+} substitution of $x = 0.01$ to 0.1 , 'a' values change from 0.4772 nm to 0.4767 nm and 'c' values change from 1.3043 nm to 1.3013 nm . The increase in the cobalt content causes a decrease in the lattice constant, indicating an increase in the crystal field around the Co^{2+} ion. This could

also be the reason for the deepening of the blue colour with an increase in cobalt doping together with the increase in CoAl_2O_4 formation¹⁰. After 7.5 atom % the change in the lattice parameters shows some discrepancy. Although the shrinkage in the 'c' parameter continues, the 'a' parameter elongates. It appears that the formation of the spinel CoAl_2O_4 which increases thereafter (Figure 4), begins to influence the hexagonal lattice of Al_2O_3 , making it more cubic ($a = 0.8103 \text{ nm}$).

The diffuse reflectance spectra of CoAl_2O_4 , $\text{Co}_x\text{Al}_{2-x}\text{O}_3$ and $\text{Co}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$ are shown in Figure 5. The electronic spectra of combustion synthesized cobalt alumina blue pigments are characterized by a broad absorption band whose

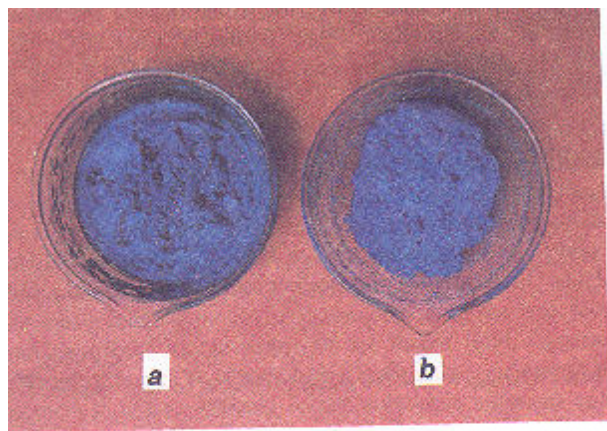


Figure 1. a. CoAl_2O_4 and b. Co^{2+} in Al_2O_3 foams.

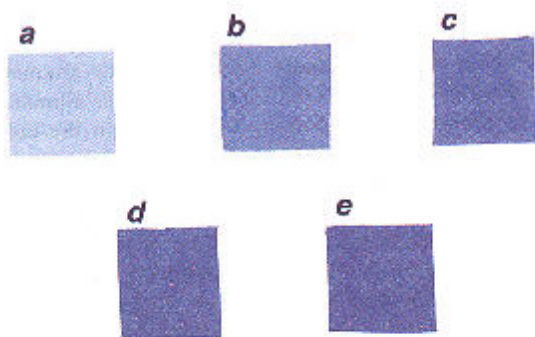
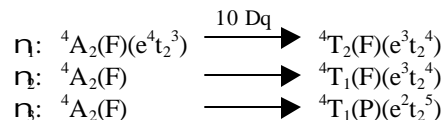


Figure 2. Variation of blue colour with Co^{2+} in Al_2O_3 ; a, 0.5 atom %; b, 2.5 atom %; c, 5 atom %; d, 7.5 atom %; e, 111 atom %.



centroid is placed in the red part of the visible spectrum. The intense convoluted absorption band with prominent absorbance peaks at around 550, 580 and 620 nm indicates tetrahedral co-ordination of Co^{2+} (ref. 11). From Tanabe Sugano energy level diagram the spin allowed Laporte forbidden d-d transitions of Co^{2+} (d^7 system) in tetrahedral coordination are¹²:



where $\eta_1 < \eta_2 < \eta_3$.

The wide and intense absorption band between 500 and 700 nm could be attributed to the third transition (η_3) from ${}^4A_2(F)$ ground state to the excited ${}^4T_1(P)$ state. The fine spectra which is diagnostic of tetrahedrally co-ordinated Co^{2+} arises due to spin orbit coupling between the excited and the neighbouring doublet states ${}^2A_1(G)$ and ${}^2T_2(G)$. Because of mixing of quartet and doublet states, the spin selection rule is relaxed and the transition is allowed¹³. The other two transitions (η_1 and η_2) are not observed as they lie

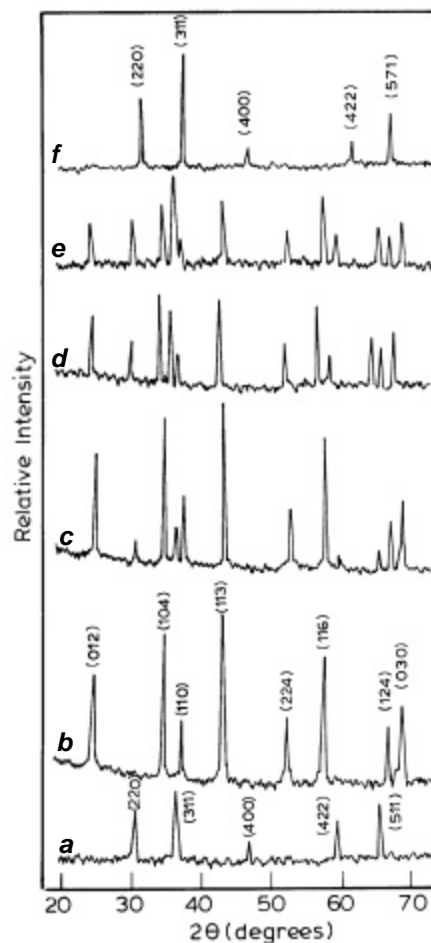
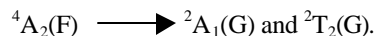


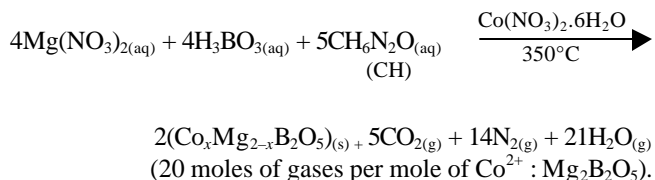
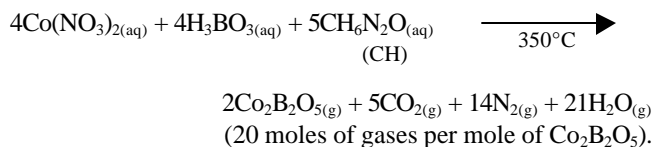
Figure 4. Powder XRD patterns of (a) CoAl_2O_4 ; (b) 0.5 atom %; (c) 2.5 atom %; (d) 7.5 atom %; (e) 10 atom % of $\text{Co}^{2+} : \text{Al}_2\text{O}_3$; (f) 2.5 atom % of $\text{Co}^{2+} : \text{ZnAl}_2\text{O}_4$.

in the far infrared region.



The spectrum is similar in all the three samples and arises due to the presence of cobalt in the tetrahedral site of the spinel CoAl_2O_4 . The $\alpha\text{-Al}_2\text{O}_3$ lattice has a hexagonal corundum structure wherein the substitution of Co^{2+} in place of Al^{3+} cannot take place due to the larger size of Co^{2+} . It therefore occupies the interstitials as CoAl_2O_4 as reported earlier¹⁴ and evident from the XRD patterns which show this spinel phase. The solid solution formed here is an inclusion type. However, in the case of ZnAl_2O_4 matrix, the substitution of Co^{2+} in the place of Zn takes place to impart the colour. The solid solution is substitution type in the spinel ZnAl_2O_4 .

Similarly, allochromatic ($\text{Co}_x\text{Mg}_{2-x}\text{B}_2\text{O}_5$) and idiochromatic ($\text{Co}_2\text{B}_2\text{O}_5$) mauve-pink (purple) pigments have been prepared as described above and characterized by their colour, XRD, IR and UV-visible spectra. The theoretical equations assuming complete combustion for the formation of $\text{Co}_2\text{B}_2\text{O}_5$ and $\text{Co}_x\text{Mg}_{2-x}\text{B}_2\text{O}_5$ can be written as:



The colour of the allochromatic $\text{Co}_x\text{Mg}_{2-x}\text{B}_2\text{O}_5$ compares well with the purple colour of $\text{Co}_2\text{B}_2\text{O}_5$ as shown in Figure 6 (5 atom % of Co doping). The as-synthesized $\text{Co}_2\text{B}_2\text{O}_5$ is X-ray amorphous. The crystalline phase occurred after sintering at 1200°C for 4 h. Powder XRD patterns of $\text{Co}_2\text{B}_2\text{O}_5$ and $\text{Co}_x\text{Mg}_{2-x}\text{B}_2\text{O}_5$ are similar to triclinic $\text{Mg}_2\text{B}_2\text{O}_5$ (Figure 7). The structure of magnesium pyroborate could be described as constructed of 2-D layers formed by the pyroborate ($\text{B}_2\text{O}_5^{4-}$) groups¹⁵. The composite ion $\text{B}_2\text{O}_5^{4-}$ is formed by two BO_3^{3-} triangles linked by one oxygen atom. The connection between the groups in the intra and inter layers is maintained by Mg^{2+} ions which are surrounded by 6 oxygen atoms forming a deformed octahedron. The strong bands at 1200 , 700 and 600 cm^{-1} in the FT-IR spectra indicate the existence of BO_3 groups in the orthoborate crystal structure.

The reflectance spectra of $\text{Co}_2\text{B}_2\text{O}_5$ and $\text{Co}_x\text{Mg}_{2-x}\text{B}_2\text{O}_5$ pigments are presented in Figure 5. The spectrum of $\text{Co}_x\text{Mg}_{2-x}\text{B}_2\text{O}_5$ is similar to that of violet-red $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ in which cobalt is octahedrally coordinated by acetate ligands. Octahedral cobalt compounds are generally pink in colour. Thus in rose-pink $\text{Co}_x\text{Mg}_{2-x}\text{B}_2\text{O}_5$, cobalt substitutes for magnesium in the octahedral lattice site of the pyroborate structure. The purple $\text{Co}_2\text{B}_2\text{O}_5$ shows a similar but a broader electronic spectrum suggesting cobalt in an octahedral environment. The band at around 560 nm for both $\text{Co}_2\text{B}_2\text{O}_5$ and $\text{Co}_x\text{Mg}_{2-x}\text{B}_2\text{O}_5$ could allowed Laporte forbidden d-d transition¹⁶.

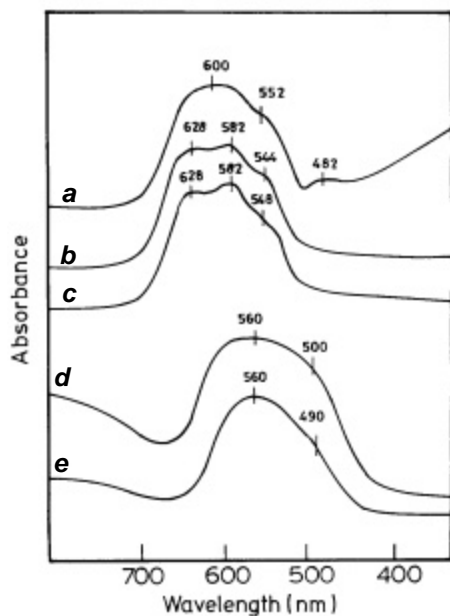
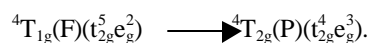


Figure 5. *a* $\alpha\text{Al}_2\text{O}_3$; *b* $\text{Co}^{2+} : \text{Mg}_2\text{B}_2\text{O}_5$; *c* $\text{Co}_2\text{B}_2\text{O}_5$; *d* $\text{Co}_x\text{Mg}_{2-x}\text{B}_2\text{O}_5$; *e* $\text{Co}_x\text{Mg}_{2-x}\text{B}_2\text{O}_5$.



Figure 6. Comparison of *(a)* $\text{Co}_2\text{B}_2\text{O}_5$ colour with *(b)* 5 atom % of Co^{2+} in $\text{Mg}_2\text{B}_2\text{O}_5$.

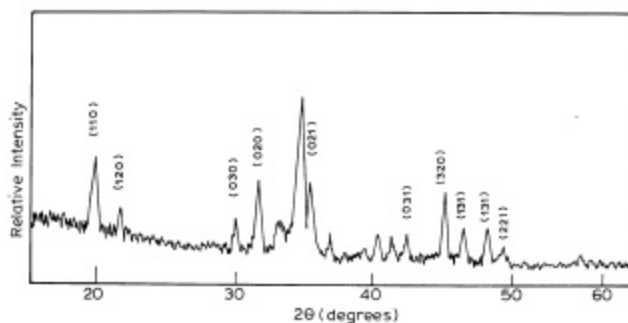


Figure 7. Powder XRD patterns of as-prepared $\text{Co}^{2+} : \text{Mg}_2\text{B}_2\text{O}_5$.

Table 2. Particulate properties of the various pigments

Pigments	Fuel	Flame temp. °C (τ)	Crystallite size from XRD (nm)	Powder density (g/cc)(\bar{V})	BET surface area (m ² /g)	Particle size from surface area (μ m)	Average agglomerate size (μ m)
CoAl ₂ O ₄ (Indigo)	CH	1100	18	2.32(53)	58	0.100	4.5
Co _x Al _{2-x} O ₃ (Blue)	Urea	1500	40	2.75(70)	10	0.220	4.0
Co ₂ B ₂ O ₅ (Purple)	CH	950	–	1.85	12	0.27	2.5
Co _x Mg _{2-x} B ₂ O ₅ (Pink)	CH	1350	15	2.1(72)	8	0.35	2.2

$x = 0.03$.

Table 3. Combustion synthesized cobalt (II) pigments

Pigments (Crystal class)	Colour	Cobalt (II) co-ordination site
Co ²⁺ : ZnB ₄ O ₇ (Metaborate)	Violet	Tetrahedral
CoAl ₂ O ₄ (Spinel)	Indigo	Tetrahedral
Co ²⁺ : ZnAl ₂ O ₄ (Spinel)	Blue	Tetrahedral
Co ²⁺ : Zn ₂ SiO ₄ (Phenacite)	Lavender	Tetrahedral
CoCr ₂ O ₄ (Spinel)	Blue-green	Tetrahedral
Co ²⁺ : ZnO (Wurtzite)	Green	Tetrahedral
Co ²⁺ : Mg ₂ B ₂ O ₅ (Pyroborate)	Rose-pink	Octahedral
Co ₂ B ₂ O ₅ (Pyroborate)	Purple	Octahedral

The particulate properties such as apparent powder densities, specific surface area, average agglomerate size of these pigments are summarized in Table 2. The fine nature of the pigments is evident from the tabulated data. The exothermicity of metal nitrate–urea reaction (> 1500°C) is quite high for the preparation of CoAl₂O₄ and borates which are unstable above 1000°C. Therefore, it was necessary to use hydrazide fuel that undergoes smouldering (flameless) combustion with metal nitrate. This method was further used to synthesize various colours of Co²⁺-based allochromatic and idiochromatic pigments as shown in Table 3.

The objectives that have been achieved through these investigations are as follows:

(i) Co²⁺-based blue and pink allochromatic pigments matching the idiochromatic pigment colours of CoAl₂O₄ and Co₂B₂O₅ have been prepared successfully by the solution combustion process. (ii) Optimum amount of Co²⁺ ions required to achieve the colour intensity of idiochromatic pigments has been determined (e.g. 5 atom % Co²⁺ in Al₂O₃/ZnAl₂O₄/Mg₂B₂O₅). (iii) The allochromatic pigments

can be made using a cheaper fuel like urea with less amount of the colouring atom, so that manufacturing cost is reduced. (iv) The solution combustion process described for the synthesis of pigments is simple, fast and energetically attractive. It has the advantage of rendering homogeneity, purity and molecular level doping of Co²⁺ (colourant) in the oxide matrices. (v) As the pigments are fine with large surface area, one needs smaller amount of these pigments to coat a given surface of the ceramic body. (vi) The process is a 'single step process' and so can be scaled up easily.

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