[J. Soc. Cosmet. Chem. Jpn.]
報 文
27(3) 304 — 313 (1993)

Black Iron Oxide Coated Thin Filler Pigments^{†1}

Tamio Noguchi

R & D Section, Merck Japan Ltd.^{†2}

Black iron oxides are used to prepare make-up products having blackish color tone.

The color of black iron oxides on the market shows yellowish and reddish black color tone. Black iron oxide is formed by the oxidation of Fe (OH)₂ obtained by mixing NaOH soln. and FeSO₄ soln.

The mechanistic study is investigated from Ferrous-Ferric Mixture by Prof. Machvec, Tamaura and Kiyama, et.al. In the wet method, several kinds of iron compounds are formed such as Fe (OH)₂, Green Rust, Fe₃O₄, FeOOH, FeOOH and Polynuclear complex containing [Fe₂ (OH)₃]³⁺ and Fe₂ (OH)₂O²⁺. It is difficult to produce black iron oxide consisting uniform particle because the particle size and the particle shape are different by the reaction condition such as concentration of alkaline solution and iron salts solution, oxidation condition of green rust containing Fe (OH)₂, kinds of iron salts and reaction temperature.

Therefore, black iron oxide having high chroma can not be produced by heterogenous precipitation method.

The chemical structure of black iron oxide is written as (FeO)_x(Fe₂O₃)_y. In black iron oxide (Fe₃O₄), the theoretical FeO content is 23.8%. The black iron oxide containing below 10% FeO, the color is brown. We have developed thin filler pigment coated with uniform black iron oxides in the crystal shape. The uniform black iron oxide were precipitated on the thin filler pigment by homogeneous precipitation using iron salts and urea. The particle size of black iron oxides on thin filler pigment depended on kinds of iron salts as raw materials. The pigment having 0.3μm of black iron oxide in mean particle size was very stable in thermal stability and very much higher in chroma. Black iron oxide coated mica having interference color were formed from hydrolysis of Iron salts using urea.

We studied to confirm the ratio of Fe (III)/Fe (II) of the formed black iron oxide by ion chromatography in comparison with the color tone of produced pigment. And the crystal structure could be analyzed by mössbauer spectrum. The black iron oxide in interference colored pigments consisted of γ-Fe₂O₃ and Fe₃O₄.

1. Introduction

Generally, the formation of black iron oxide, such as Fe₃O₄, γ-FeOOH, has been performed by means of wet method, such as hydrolysis and oxidation of ferrous (II) salts solution¹⁾. The color tone

is affected by the particle size, the shape of crystal and ferrous oxide content in total iron of black iron oxide. Black iron oxide is formed from ferrous ion and ferric hydroxide in alkaline suspension.

And the formula of Fe₃O₄ which is prepared by

^{†1} 第17回 IFSCC 横浜大会 ('92年10月) で口頭発表

^{†2} 51-15 Aza Egoshi, Kurosuno Izumi-cho, Iwaki-shi, Fukushima 970-04 Japan

mixing of NaOH and FeSO_4 , and subsequent oxidation of the precipitate was studied.

The reaction mechanism is investigated from Ferrous-Ferric Mixture by Prof. Machvec, Tamaura and Kiyama, et al²⁻⁵. In these wet methods, several kinds of iron compounds are formed such as $\text{Fe}(\text{OH})_2$, Green Rust, Fe_3O_4 , αFeOOH , βFeOOH and polynuclear complex containing $[\text{Fe}_2(\text{OH})_3]^{3+}$ and $[\text{Fe}_2(\text{OH})_2\text{O}]^{2+}$.

An overview of possible interconversions is presented in Fig.-1.

Fig.-1 Schematic representation of formation and transformation pathways of common iron oxides together with the approximate transformation conditions.

In black iron oxide (Fe_3O_4), the theoretical FeO content is 23.8%. The black iron oxide containing below 10% FeO, the color is brown. And the for-

mula would be written as follows:

It is difficult to produce black iron oxide consisting of uniform particles because the particle size and the particle shape is influenced by the reaction condition such as concentration of alkaline solution and iron salts solution, oxidation condition of green rust containing $\text{Fe}(\text{OH})_2$, kinds of iron salts and reaction temperature.

Therefore, black iron oxide having high chroma can not be produced by heterogenous precipitation method⁶⁻⁸. In this study, the preparation method is described, which make it possible to obtain black iron oxide of narrow size distribution and of uniform shape on mica by homogeneous precipitation. And the black iron oxide coated mica having interference color is formed by the preparation method. The crystal structure of black iron oxide on mica is identified to consist of Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ by mössbauer spectrum⁹⁻¹³.

2. Experiment

2.1 Material

Chemical reagents of analytical grade were used. The thin filler substrate used were Mica, Talc, Sericite, Kaoline and Titaneous-mica.

2.2 Procedure

Mica is suspended into deionized water and added urea, ferrous, ferric salts and potassium nitrate solution into the suspension. The suspensions were heated to 95°C within 1.5 hr and the temperature was kept constant during the precipitation of Fe_3O_4 on mica. The product was collected on filter paper, washed with water and then dried at about 100°C .

2.3 Analysis of Products

The amounts of ferrous and ferric ions were determined by Shimadzu ion chromatography model HIC-6A. The ratio of Fe(III)/Fe(II) of solid products were determined by Mössbauer spectrum.

2.4 Crystal Structure and Composition

Crystal structure was confirmed by powder X-ray analyzer. Crystal forms and surface condition were observed by scanning electron microscope of Hitachi Seisakusho model S-800. And its composition was analyzed by EDX of Horiba model EMAX-2700.

2.5 Thermalstability

The thermalstability of products was confirmed by TGA and DTA of Seiko Denshi model SSC5200. The change in color of the products heated for 24 hours in atmosphere at temperatures of 100, 120, 140, 160°C was measured by Hunter L.a.b. color meter.

2.6 Particle Size Distribution

Particle size distrubution was measured by Cilas model 715.

2.7 Color Measurement

Color of products were measured using a spectrophotometric colorimeter (Hunter L.a.b.). The color was measured at 0°/+45° on white draw down cards and 0°/+45°, -22.5°/+22.5° on black draw down cards.

Murakami goniospectrophotometer model GCMS-3 was used to measure the optical behavior of pearlescent and interference type pigment.

3. Results and Discussion

3.1 Formation of Black Iron Oxide Coated Mica

The pigments were formed by precipitating black iron oxide on to mica surface which was made from thermal hydrolysis decomposition of urea with ferrous salts using potassium nitrate as oxidants on mica^{14),15)}.

Table-1 shows L.a.b. value of black iron oxide coated mica produced by using several kinds of ferrous salts.

Table-1 L.a.b. values of iron black coated mica and the mean particle size of black iron oxide on mica

Fe Salts	45°/0°(White)			Hiding Power of black iron oxide (μm)	Particle size
	L	a	b		
FeSO ₄ ·7H ₂ O	30.2	0.3	0.9	15.6	0.3
FeSO ₄ (NH ₄) ₂ SO ₄	19.2	3.1	5.3	61.3	0.1
FeCl ₂ ·4H ₂ O	20.0	2.3	4.3	54.9	0.1
FeBr ₂ ·2H ₂ O	25.0	5.4	9.3	44.4	0.1

The crystal shape of black iron oxides were influenced by kinds of ferrous salts used. Black iron oxide of large particle size was formed from ferrous sulphate. The color tone showed most blackish color tone among them. **Figure-2** shows the photographs of SEM of black iron oxide coated mica formed from ferrous sulphate and ammonium ferrous sulphate.

It was observed in SEM photographs that black iron oxides of uniform shape were scattered on mica. The particle size of black iron oxide (a) formed from FeSO₄ was larger than that of black iron oxide (b) formed from FeSO₄(NH₄)₂SO₄. The reason seems to me that the crystal growth of black iron oxide (a) is more rapid than the adsorption rate of black iron oxide (a) on mica. On the other hand, the adsorption rate of black iron oxide (b) is more rapid than the crystal growth of black iron oxide (b). In some paper, the chemical structure of black iron oxide is written as (FeO)_x(Fe₂O₃)_y. Therefore, the color of black iron oxide is affected by Fe(II) content in total iron of black iron oxide. Then, Fe(II) content in these products was analyzed by ion chromatography.

As a result, Fe(II) content of the product formed from ferrous sulphate was more than that of other products. From these results, it was confirmed that Fe(II) content and the particle size are a key factor for the blackish color tone of black iron oxide coated mica. **Fig.-3** shows TGA and DTA curves

Fig.-2 Electron micrograph of black iron oxide coated mica
 2-a : Iron black on mica formed from FeSO_4
 2-b : Iron black on mica formed from $\text{FeSO}_4 (\text{NH}_4)_2 \text{SO}_4$

of produced black iron oxide coated mica. The product formed from FeSO_4 was more stable in the thermal stability than that of any other products.

3.2 Formation of red iron oxide coated mica

The red iron oxide is produced from calcination of synthetic black iron oxide. (1) The following

Fig.-3 TGA and DTA curves of black iron oxide coated mica
 — : Pigment formed from FeSO_4
 - - - : Pigment formed from $\text{FeSO}_4 (\text{NH}_4)_2 \text{SO}_4$

equation represents the reaction involved in this process.

Produced black iron oxide coated mica was calcined at 800°C for producing red iron oxide mica for the purpose of investigating the color purity of these products. Many colored pigments (Orange, Red, Violet) could be prepared from black iron oxide coated mica having different particle size of black iron oxide. **Table-2** shows L.a.b. values of red iron oxide coated mica prepared from

Table-2 L.a.b. values of Red Iron Oxide coated Mica

Fe Salts	45°/0°(White)			Hiding Power	Particle size of black iron oxide (μm)
	L	a	b		
FeSO ₄ •7H ₂ O	39.1	21.9	9.8	24.5	0.3
FeSO ₄ (NH ₄) ₂ SO ₄	38.1	31.7	20.6	50.2	0.1
FeCl ₂ •4H ₂ O	37.4	34.2	18.8	47.0	0.1
FeBr ₂ •2H ₂ O	40.3	36.9	22.9	44.7	0.1

black iron oxide coated mica.

And **Fig.-4** shows the chroma of these products in comparison with the chroma of commercial red iron oxide.

The comparative data were prepared from the chroma of skin color having the same color tone in the munsell value. These skin colored pigments were made by mixing red iron oxide and yellow iron oxide as follows:

Skin Color-(1)

Pigment	Mixing ratio			
	a	b	c	d
Fe ₂ O ₃ coated Mica	3	2	4	5
FeOOH coated Mica* ¹	3	2	4	5

Skin Color-(2)

Pigment	Mixing ratio		
	e	f	g
red iron oxide* ²	1	0.75	0.5
yellow iron oxide* ³	1	0.75	0.5

*¹: FeOOH coated Mica was prepared by depositing FeOOH formed from Ferric ammonium sulphate and urea on mica

*^{2,3}: commercial pigment

Fig.-4 The comparative data of chroma data of chroma between iron oxide coated mica and commercial red iron oxide

The chroma of skin color-(1) was better than that of skin color-(2) because the red iron oxide on mica had uniform particles and shape. The chroma of these skin colored pigments was measured by Murakami goniospectrophotometer GCMS-3.

3.3 Black Iron Oxide Coated Thin Filler Pigment

Black iron oxide produced from ferrous sulfate and urea was deposited on the surface of other materials such as synthesis mica, sericite, talc, kaoline and titanium oxide-coated mica commercially available as a pearl pigment. The crystal shape of black iron oxide on synthetic mica was the same as that of black iron oxide on mica. The particle size of black iron oxide on kaoline was smaller than that of black iron oxide on mica. The shapes of black iron oxide particles deposited on sericite were spherical.

Such spherical particles grown by agglomerating

fine particles of black iron oxide could be deposited on the surface of titanium oxide-coated mica. The growth of particle of black iron oxide depends upon the properties of the surface of flaky substrate. Maybe this is attributed to the oriented overgrowth caused by the growth of a crystal phase in a specified direction on the surface of other crystal phase or the epitaxy. Fig.-5 shows these SEM photographs.

Table-3 shows Hunter L.a.b. value of black iron oxide coated thin filler pigment.

3.4 Black Iron Oxide Coated Mica Having Interference Color

Black iron oxide coated mica having interference color could be obtained by hydrolizing ferrous salts, ferric salts and urea in the mica suspension. The interference colors of produced pigments changed by mixed ratio of Fe(III)/Fe(II).

Fig.-5 Electron micrographs of black iron oxide coated thin filler pigments.

Table-3 L.a.b. values of black iron oxide coated thin filler pigment

Sample	45°/0° (Black)			45°/0° (White)		
	L	a	b	L	a	b
MP115*-F20	61.4	-0.6	-1.4	58.9	-0.9	-2.4
Timiron** B-F20	53.9	1.3	-15.0	44.6	2.3	-24.6
Mica-F20	39.1	0.4	-0.1	33.3	0.3	-0.6
Sericite-F20	28.8	1.1	1.1	28.5	0.7	0.7
Talc-F20	29.5	1.3	3.2	27.6	0.5	1.9
Kaolin-F20	27.5	1.7	1.9	26.5	0.9	0.8

* MP-115 : Silver titanous mica

** Timiron B : Blue titanous mica

Figure-6 shows the relationship between L.a.b. value and the mixing ratio of Fe (III)/Fe(II). And it was confirmed that small amount of ferric salts is necessary to obtain the interference color of black iron oxide coated mica.

The interference color changed, with the increa-

se of the quantity of black iron oxide, to gold, violet, blue and green.

Fig.-7 shows the chromaticity coordinates of interference film prepared by black iron oxide coated mica.

Fig.-8 illustrated a varied-angle spectral distribution. This is the spectral distribution of the reflected light obtained by changing the angle of incident light at an angle of -45 degrees on the black iron oxide-coated mica with the interference red color applied to a white card and a black card. The samples show the same color tone on both white and black cards.

The interference color of obtained pigment changed by changing heating temperature. Some pigments having blue interference color at 120°C changed to green interference color at 160°C. Then, the ratio of Fe(III)/Fe(II) of these pigments were investigated by Mössbauer spectrum.

Fig.-6 The relationship between L.a.b. values and the mixed ratio of Fe(III)/Fe(II)

Fig.-7 The chromaticity coordinates of interference film prepared by black iron oxide coated mica

○ : a.b. values on white card by changing quantity of Fe_3O_4
 ● : a.b. values on black card by changing quantity of Fe_3O_4

Fig.-8 Directional spectral reflectance factor distribution of an interferenced pigment

Fig.-9 and, **Fig.-10** show the analysis data by Mössbauer spectrum. The treated pigment at 120°C was mostly Fe_3O_4 and the treated pigment at 160°C was mixed product of Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$.

Table-4 shows the analysis results by Mössbauer spectrum.

Table-4 Mössbauer analysis results of black iron oxide coated mica in comparison with standard of black iron oxide

	Interference Blue at 120°C	Interference Green at 160°C	Standard Fe_3O_4 $\gamma\text{Fe}_2\text{O}_3$	
$\gamma\text{-Fe}_2\text{O}_3$	31	59	17(0)	100
Fe_3O_4	69	41	83(100)	0
Fe^{2+}	23	14	28(33)	0
Fe^{3+}	77	86	72(67)	100

Fig.-9 Mössbauer spectra of Interference Blue pigment

Fig.-10 Mössbauer spectra of Interference Green pigment

As a results, it was confirmed that the interference color is formed from $\gamma\text{Fe}_2\text{O}_3$ and Fe_3O_4 on mica. The interference color changed with an increase in $\gamma\text{-Fe}_2\text{O}_3$ on mica because the refractive index of $\gamma\text{-Fe}_2\text{O}_3$ is higher than that of Fe_3O_4 . ($\gamma\text{-Fe}_2\text{O}_3$, $n=3.0$, Fe_3O_4 , $n=2.4$)

Fig.-11 is the SEM photograph of black iron oxide coated mica having interference color Blue.

4. Conclusion

Uniform particles of black iron oxide could be obtained on the thin filler surface by thermalhydrolysis of ferrous salts using urea in the presence of oxidant in the thin filler pigment

Fig.-11 Electron Micrograph of black iron oxide coated mica having interference color blue

suspension.

The obtained black iron oxide coated thin filler pigment was blackish powder and the pigments had good thermalstability.

Red iron oxide coated mica having high chroma was produced by calcination of black iron oxide coated mica.

Black iron oxide coated mica having interference color was produced by coating the black iron oxide formed from coprecipitation of both ferrous hydroxide and ferric hydroxide on mica. It was determined by Mössbauer spectrum that the crystal structure of black iron oxide on mica was Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$. These pigments can be applied for coloring of make-up proudcts and foundation cake.

In this study, three kinds of black iron oxide coated thin filler pigment were prepared by homogeneous precipitation method. The drawings of the structure of these pigments are shown in Fig.-12.

Fig.-12.

REFERENCES

- David P. Keller, "Synthetic, Colored Iron Oxide Pigments", in Pigments Handbook, Vol. I, Wiley Interscience, Ohio 1987
- T. Sugimoto, and Matijevic, E., J. Colloid Interface Sci, **74**, 227 (1980)
- M. Kiyama, Bull. Chem. Soc. Japan, **47**, 1646 (1974)
- Y.Tamaure, K.Ito and T.Katsura, J.Chem. Soc. Dalton Tsans., 189 (1983)
- S. Miyamoto, Bull. Chem. Soc. Japan, **2**, 40 (1927)
- Willard, H.H., and Tang, N.K., J. Am. Chem. Soc., **59**, 1190 (1937)
- A. Kato, and Y. Morimitsu, The Chemical Society of Japan 800 (6) (1984)
- K. Matsuda, M. Sumida, K. Fujita, and S. Matsuzawa Bull. Chem. Soc. Japan, **60**, 4441 (1987)
- E. Tronc, J-P. Jolivet, and J. Livage, J. Chem. Research, 136 (1987)
- Gibb, T.C. (1976) Principles of Mössbauer spectroscopy Chapman & Hall, London, 254 pp
- Murad, E. and Johnsohn, J.H. (1987) Iron Oxides and oxyhydroxides In G.J. Long (Ed) Mössbauer spectroscopy
- E. Murad and U. Schwertmann Amer. Mineralogist **65**, 1044 (1980)
- E.Murad and U.Schwertmann Clay Min. **18**, 301 (1983)
- T. Noguchi, T. Watanabe and A. Mizuguchi 1985 Shikizai Technical Conference on Japan Society of Colour Material p.47
- T. Watanabe and T. Noguchi, United States Patent 4, 435, 220 (1993年1月15日受理)

Fig.-12 The drawing of the structure of prepared black iron oxide coated thin filler pigments