

Micaceous iron oxide (MIO)-pigmented undercoats and finishes applied over suitable primers have been used extensively for over a century in Europe and many other parts of the world to provide long-term corrosion prevention for structural steel work.^{1,2} Structures protected today with MIO paint systems include bridges, electric transmission towers, radio masts, railway gantries, cranes, building frameworks, gas holders, fuel tanks, chemical plants, storage tanks, pipework, harbor facilities, and offshore platforms.¹⁻¹⁶

The protective properties of MIO derive from its flake-like particle structure and chemical inertness. For optimum performance, the particle size range and flake thickness are critical. The effectiveness of MIO pigments in providing maximum durability has been established by several authorities and has been well documented.

Conventional MIO paints based on drying oil media continue to give excellent service, but more advanced coatings are now available to cope with the increasingly demanding requirements of modern industry. These days, MIO is a valuable ingredient in high performance coatings based on modified alkyds, phenolic resins, acrylics, vinyl copolymers, chlorinated rubber, two-pack epoxy resins, moisture-curing urethanes, and many other binders.^{1,3-7,9-14,17,18}

Although MIO is used mainly in barrier-type intermediate coats and topcoats in conjunction with anti-

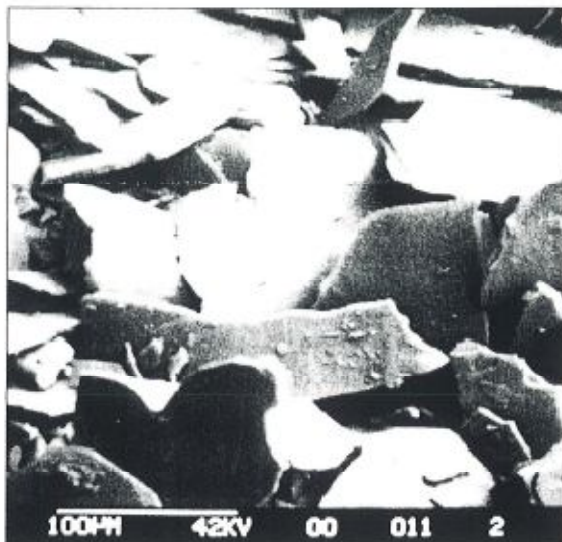


Fig. 1 - SEM of naturally occurring MIO pigment standard grade exhibiting distinct, thin lamellar morphology. Photos courtesy of S. Wiktorek.

corrosion primers, it can also be incorporated in high-build primers for direct application to metal surfaces.^{4,5,7-10,12,15,16}

Most industrial facilities in Australia are close to the coast, and steel structures and equipment are exposed to severe conditions including marine, heavy industrial, light industrial, and chemical environments. In addition, ultraviolet light ray concentrations are very high, attacking almost all kinds of organic coatings. MIO-pigmented paints have been widely used in Australia for several decades with outstanding performance in all existing severe conditions, including jetty piles exposed to marine environments.^{12,14-16}

Examples of outstanding MIO coating performance are the Hawkesbury River Bridge in New South Wales and the Sydney Harbour Bridge. In 1909, 12 megagrams

(13 tons) of MIO paints were purchased for the repainting of the Hawkesbury Bridge.² The coating had a covering power of 11,925 sq m per megagram (141,400 sq ft per ton). The Sydney Harbour Bridge was constructed in 1932 using 50,000 megagrams (55,000 tons) of steel. This structure, which carries both road and rail traffic, has been protected with MIO-pigmented coatings since it was built.^{12,15,16}

Although MIO has been around for a long time, protective coatings containing MIO have been continuously updated to suit requirements of increasing severity and are available in the most advanced types of coatings.¹⁸ Of course, the nature of the environment and the required length of protection govern the final selection of the paint medium.^{1,3} Regardless of the resin or paint

1975 North Hawthorne Avenue *continued*

medium, the ability to withstand severe weathering for extremely long periods is a unique feature of MIO-pigmented coatings. In addition, extensive accelerated laboratory tests on cathodic disbondment have proved that carefully formulated MIO coatings based on epoxy resins are compatible with cathodic protection in the form of sacrificial anodes or impressed current.¹⁹

Synthetic MIO

In the UK, attempts have been made over a number of years to synthetically produce MIO. These attempts eventually resulted in the commercial development of a synthetic MIO pigment. To promote this new product, the technical staff of one manufacturer has recently published several papers claiming superiority of the synthetic MIO compared to the naturally occurring MIO pigment.

To investigate such claims, a comparative microscopic examination of natural and synthetic MIO pigments has been carried out by independent specialists in Australia. Participating in the research were a consulting firm for process mineralogy; the metallographic investigations department of an Australian steel company; an Australian coating manufacturer; and the author, formerly with BHP Steel International in Australia and now a private consultant in corrosion technology.

One sample of MIO pigment comprised a processed, naturally occurring MIO. The second sample was of a synthetically produced MIO. According to established criteria, both of these materials satisfied requirements for pigment-grade MIO. Although the methods in this study followed the procedures outlined in the relevant standards, a comparative evaluation required more extensive examination procedures.

This article outlines the procedures followed for the comparative microscopic examination of the MIO

pigments in question. It also reviews the cross section examination of the epoxy resin-based MIO coatings applied to a steel substrate and provides details of the results.

Structure, Shape, and Color of MIO Particles

When a test portion of the pigment is viewed under a scanning electron microscope (SEM) using a magnification of about 250x, the structure of the particles corresponds to the lamellar structure shown in Fig. 1. When a test portion of the pigment is viewed by means of transmitted light and an optical microscope using a magnification of about 200x, the particles are shown to consist of sharply defined, angular, ruby red translucent platelets with clearly defined fracture planes.^{2,7,15,20}

Characteristics of MIO Pigment

MIO is a natural mineral ore known as specular hematite. It is metallic gray and is similar in crystal habit to mica, which gives rise to the description "micaceous."^{1-3,5,10,14-16,21} Its distinguishing feature is a tabular crystal form, which can be easily fractured to give very thin platelets of good chemical stability even at high temperatures.^{2-4,12,14-16,22} Suitable processing of the crude ore produces the required size range of gray, flake-shaped specular particles. They are composed mainly of Fe_2O_3 , which is used as pigment in the paint industry.^{10,12,15,16,24}

Although MIO is found in various parts of the world, the actual particle morphology, following processing, may not be micaceous. MIO pigments can vary in composition, particle size range, and particle shape depending on whether they are produced synthetically or, in the case of refined natural oxide, on the location where the ore was mined. The ore used in protective coatings should contain at least 85 percent

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Fe_2O_3 and an extremely low amount of water-soluble salts, and have a fully developed lamellar structure.^{1-3,10,15,21,23}

Microscopic examination of MIO pigment from various deposits reveals that the particle shape can range from flake-like (varying in thickness) to completely granular.^{2,7,12,15,16} Some pigments consist of fines and variously shaped particles. The world standard for MIO today is the Waldenstein region source between the provinces of Corinthia and Styria in Austria.² This is the largest and best known deposit of MIO, and the quality and quantity of the as-mined ore are unique.^{1,3,5,14,15,21,22,24} The ultrathin flake structure and "soft" texture is a notable feature of Austrian MIO.⁵ The Austrian standard grade is similar to that found in the earlier English "Great Rock Mine" in South Devon (no longer available commercially).^{2,3,8}

In the last few years, several alternatives, including synthetic MIO (Fig. 2) have become commercially available. These alternatives, however, have obvious differences in their physical properties. To ensure that a high level of corrosion prevention is maintained, it is necessary to characterize the physical properties of the alternatives and evaluate their effect on the corrosion protection of steel.^{7,14,15,21}

Mechanism of Protection

The protective action of MIO is ascribed to close packing of the pigment platelets within the paint film. The platelets form overlapping and interleaving multi-layers, positioned roughly parallel to the coated substrate.^{5,10,21,25,26} including the edges (Fig. 3).^{12,14-16,21} At optimum pigment volume concentration (PVC), the pigment layers form a tough, lamellar seal that acts as an effective barrier. The layers impede penetration of moisture,²⁸ / *Journal of Protective Coatings & Linings*

gases, and corrosion promoters (and, hence, increase corrosion protection); improve film strength; reduce polymer swelling; and minimize blistering.^{1,5,9,12,27} Moisture vapor can penetrate the paint film, but the lamellar network structure also permits vapor to be dissipated without forming blisters (Fig. 4).²⁴

The pigment flakes also provide mechanical reinforcement and a stress-relieving effect that result in enhanced cohesion and film integrity. MIO improves adhesion, application tolerance, recoatability, and en-

vironmental resistance of heavy-duty industrial coatings. It also improves abrasion and chemical resistance. The flaky particles on the upper surface shield the medium underneath from ultraviolet degradation and other agents that lead to paint film deterioration.^{1,2,5,10,12,22,25,26} Should the upper surface of the coating be damaged, successive layers of pigment will present themselves to the atmosphere as barriers to actinic radiation and moisture penetration, thereby preserving the effectiveness of the film.¹ This leaf-

Fig. 2 - SEM of synthetic MIO showing limited development of distinct lamellar morphology. High content of line irregular material is present along with acicular forms.

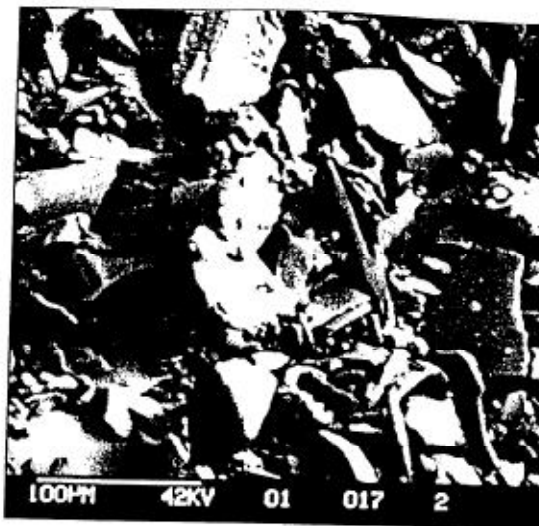
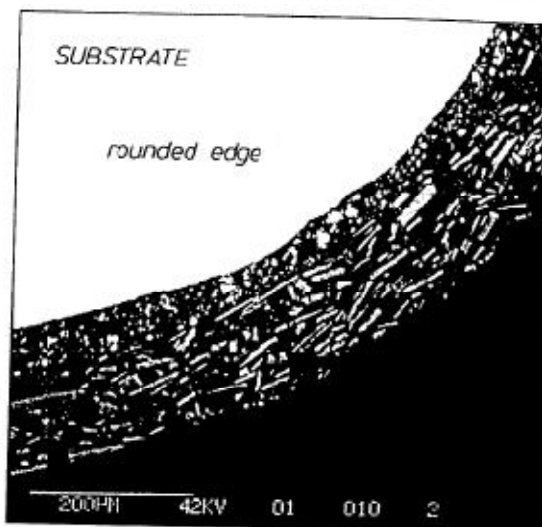


Fig. 3 - SEM illustrating the coating thickness and the orientation of naturally occurring MIO pigment on a rounded edge.



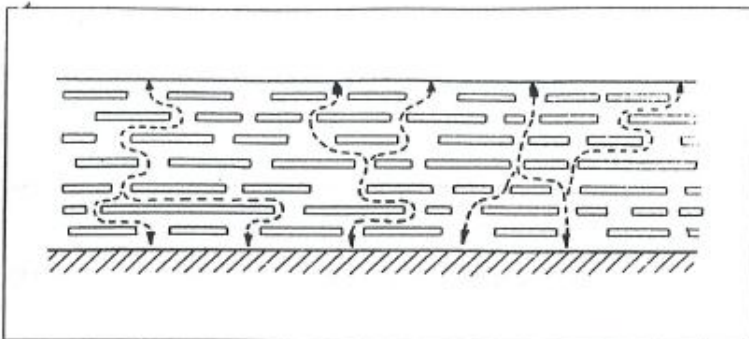


Fig. 4 - Diagram of coating containing lamellar-shaped MIO showing how pigment layers impede penetration of moisture and pollution. The interleaving particles also reinforce and strengthen the paint film. Moisture vapor can penetrate, but the structure also permits vapor to be dissipated without forming blisters.

ing prevents chalking and film erosion, and maintains the protective action of the medium.

With the introduction of airless spray painting techniques, the protective properties of MIO-pigmented paints are remarkably improved, since more regular and more even coatings can be achieved. Airless spray painting results in better flow of sprayed paint compared to brush application. The movement of a coating during and after application and before the film is formed assists the flaky MIO particles in achieving parallel orientation. However, for maximum benefit, the paint should be vigorously applied so that the flaky particles can easily align themselves in overlapping layers and thus permit the pigment to exert its full protective value. It is believed that such MIO platelet arrangements in applied coatings are a function and interaction of flake thickness, weight, size, and density.¹

Examination Procedure

Preparation of Slides

The preparation procedure adopted for the examination involved oil immersion slides as normally used in conjunction with AS 2855-1986.²⁰ The same procedure is also recommended in ISO 10601:1993(E).²³ The "dry" slide examination procedure in

the ISO standard was not adopted because the material clustered significantly across the slide. This clustering was more pronounced with the finer materials. As a result, the suitably dispersed portion was not found to be representative.

During initial slide preparation, the behavior of the 2 sample materials differed. Following initial placement of the cover slip, maximum sample dispersion was facilitated by applying a circular movement to the cover slip, under light pressure. This procedure thus yielded the development of a near monolayer of particles for observation. During preparation of the naturally occurring MIO, movement of the cover slip was generally smooth, with increasing stiffness (an effect of surface tension) as the material was dispersed. The synthetic MIO gave a gritty feel to the cover glass motion and did not develop the stiffness found with the naturally occurring MIO.

Examination of the synthetic MIO sample suggested that this behavior was accounted for by equi-dimensional (i.e., non-lamellar) gangue (rock) and iron oxide particles, in particular, those associated with the coarser end of the size distribution.

Both the natural and synthetic MIO samples were screened to provide 3 size fractions (+53, -53 +38,

and -38 micron). The screening comprised an initial dry separation, followed by wet spray rinsing of the +53 and +38 screen contents. The 3 size fractions from each sample were dried and weighed.

Preparation of the oil immersion slides was carried out for each size fraction using progressive random increment sampling methods. These methods were previously used for fine materials and had been shown to produce good repeatability. The behavior of the predominant finer size fraction of the synthetic MIO showed a marked improvement in distribution and dispersion.

Examination and Evaluation

Assessment of the MIO materials was aimed at determining the relative differences in content of thin iron oxide lamella. The basic features shown in Table 1 were adopted for assessment. Each could be assessed with reasonable consistency and provided the basis for comparison between the 2 MIO materials.

The contents of each constituent (Table 1) for each of the size fractions were determined using petrographic point counting procedures. An automatic mechanical stage and counter was used. Duplicate preparations were counted, and 600 to 800 constituent particles or points per slide were assessed. For each analysis, the magnification and illumination conditions originally used for determining the characteristics of the components were kept constant.

This comparative evaluation also included SEM photomicrographs of typical areas from each sample at a standard 250x magnification to illustrate the comparison of particle morphology through photomicrography. Cross-sectional photomicrographs of coated test panels are also included in this comparative examination procedure. These panels show the typical features exhibited by the natural

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**Table 1
Constituents of the MIO Samples Tested**

Component	Description
Translucent Lamella	Type A—thin, clear red lamellae with slightly granular appearance, associated with iron oxide platelets Type B—distinct ruby red, tending towards deeper blood red coloration at the thicker end of the translucent range of platelet thickness
Brown Lamellar	Thin, brown with a very slight red tinge; tends toward opaque character
Opagues	Black, opaque grains representing very thick platelets or granular material; no judgement on relative thickness can be made; does not conform to a micaceous or lamellar morphology
Gangue	Non-iron oxide components, comprises various silicates, carbonates, and other mineral components; translucent with varying optical anisotropy and coloration; not differentiated
Other	Any significant features or components not attributable to the above categories

**Table 2
Weight Percent of MIO Retained by Sieve Size**

Sieve Size micrometers (mils)	Wt. Percent Retained	
	Natural MIO	Synthetic MIO
-105 [4]	0	0
+53 [2]	27	12
+38 [1.5]	18	7
-38 [-1.5]*	55	81

*Residual or undersize

MIO and the synthetic MIO pigments within the applied coating.

Results and Discussion

Table 2 gives the weight percent retained for each MIO material for the separate size fractions used to determine the relative content of the components (Table 1).

Table 3 shows the results of the quantitative point count analysis for the 3 size fractions. For each sample, the analysis for the original or as-received sample was calculated from the individual size fraction results. From the results, the following comments can be made.

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Table 3
Quantitative Volume Analysis

Size Fraction	Wt. Percent Retained	Translucent Lamella		Volume Percent			
		Type A	Type B	Brown Lamella (Thick Platelets)	Opaque (Black)	Gangue	Other
Natural MIO							
53 μm	12	35					
-53 +38 μm	18	29	47	9	15	5	0
	55	28					
Full Sample	100	30.3	38.5	6.8	17.5	6.9	
Synthetic MIO							
53 μm	2	7					
-53 +38 μm	7	14	20	9	56	6	0
	81	11					
Full Sample	100	26.3	24.9	2.0	41.3	4.6	0.8

*Acicular or needle-like morphology

• The naturally occurring MIO exhibits a much wider size distribution than the synthetic MIO, with around 45 percent of the particles greater than 38 micrometers (1.5 mils). The content of thin, translucent lamella (Type A and B) is uniformly distributed across the full size range at levels of 65 to 71 percent (Fig. 5). The -38 micron natural MIO (55 percent) has a higher content of translucent lamellar with a much lower content of superfine and irregular shaped particles than the synthetic MIO.

• The synthetic MIO comprises a much narrower size range than the naturally occurring MIO with 81 percent of the particles less than 38 micrometers (1.5 mils). Within this size fraction, the content of translucent lamella is relatively high at around

59 percent. This content, however, is 11 percent lower than the natural MIO for the same size fraction. The average size of the material within this size fraction appears to be smaller for the synthetic MIO than for the naturally occurring MIO. For the size fractions greater than 38 micrometers (1.5 mils), approximately 19 percent of the total material, the synthetic MIO is dominated by opaque material with a relatively low content of translucent lamella (Fig. 6).

Figures 7 and 8 illustrate the typical features of the representative MIO materials in an applied coating. The photomicrographs are representative of cross sections from test panels. The MIO materials were prepared using an epoxy resin base and

applied to the test panels. All aspects of the preparation of MIO-pigmented paint and its application were closely supervised by technical personnel. Average coating thickness ranged between 120 and 140 micrometers (5 and 6 mils). The figures show the differences in size, distribution, and the degree of lamellar or micaceous character exhibited by the 2 MIO materials.

Conclusion

Results of the above evaluation show that the naturally occurring MIO material exhibits a far more well developed micaceous morphology than the synthetic MIO. The naturally occurring MIO is characterized by a wide size distribution and a uniform content of well defined,



Fig. 5 - Naturally occurring MIO -53+38 micrometer fraction (oil immersion, transmitted light). Sample exhibits uniform content of thin lamellar micaceous iron oxide.

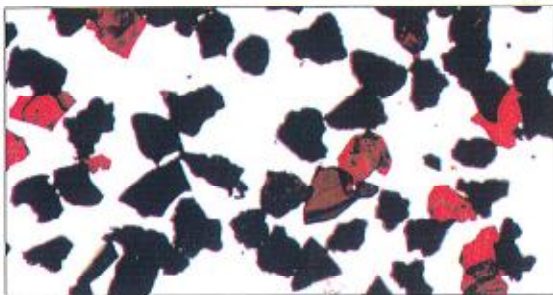


Fig. 6 - Synthetic MIO -53+38 micrometer fraction (oil immersion, transmitted light). Sample exhibits dominant opaque material with relatively low content of acceptable translucent lamellar shaped platelets.



Fig. 7 - Cross section of test panel coated with naturally occurring MIO, MIO platelets exhibit a consistent tendency towards parallel to sub-parallel orientation with respect to the steel substrate.



Fig. 8 - Cross section of test panel coated with synthetic MIO. Fine MIO platelets together with the more granular iron oxide components exhibit a more random orientation within the coating layer. Extended parallel or sub-parallel orientation of the MIO component was generally absent throughout all of the cross sections examined.

thin micaceous iron oxide lamella across the full size range.

The distribution and orientation of naturally occurring MIO pigment in the applied coating, even on the edges, provides maximum protection to the substrate. The synthetic MIO is much finer than the naturally occurring MIO, with both the major proportion in terms of size and acceptable lamella thickness at less than 38 micrometers (1.5 mils).

Relatively large proportions of superfine particles are present in the examined synthetic MIO. Such superfines may not conform to a micaceous or lamellar morphology. The equi-dimensional or non-lamellar shaped particles dominating in fractions greater than 38 micrometers (1.5 mils) may reduce the effectiveness of applied coatings considerably. The equi-dimensional shaped (opaque) material reduces the bulk (volume) of lamellar pigment, and, consequently, proportionately fewer protective platelets of MIO are distributed within the applied coating (Fig. 8). Such granular-shaped particles associated with the coarser end of the size distribution may interrupt the development of parallel orientation of the lamellar-shaped platelets.

Finally, microscopic examination of a sample of a synthetic MIO provided sufficient information to conclude that this material would have difficulty in conforming to the requirements prescribed by Australian Standard 2855-1986. Therefore, the synthetic MIO must be considered unsuitable for use as a pigment in industrial coatings for long-term protection, especially in severe, corrosive environments. Initial results of current comparative weathering tests (6 months exposure), within a coastal environment, would appear to confirm this view. Results of these weathering tests will be made available for publication soon.

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