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TECHNOLOGY FOR MIO PRODUCTION

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ABSTRACT
MIO is natural iron oxide pigment with specific flaky or plate forms of the particles (Micaceous Iron Oxide). It is widely used in anticorrosive coverings. It has no competition against aggressive mediums and ultraviolet radiation.
Raw material for production of MIO is sized in Kremikovtzi mineral deposit. Characteristic parameters for production of such pigment were set by laboratory experiments. A technological flowsheet for obtaining of quality MIO type pigment according to the international standards were drawn up.

MIO - ESSENCE AND USEAGE

The name MIO leads its beginning from the abbreviation of Micaceous Iron Oxide. As it was underlined by John Benbow the name does not have connection with the mica. Micaceous is used to emphasize the plate shape of the different particles which are usually in size of 10 µm to 100 µm with thickness about 5 µm. Taking into account the morphology of these particles, used as a covering they align parallel to the surface they are laid. This is the main characteristic of the MIO type pigments. Fe_2O_3 is not soluble in water, organic solvents, alkali. It is not toxic. It is stable under temperature variations, not corrodible. These facts indisputably show that these pigments based on Fe_2O_3 are priceless as anticorrosive coverings.

MIO is a crystalline form of Fe_2O_3 that differs from the more popular red, yellow and brown pigments. The mineral is known as specular hematite and has the same chemical content as hematite but crystallizes in different crystal form. The growth of the crystalline forms of the hematite is clearly connected to the crystallization conditions: contactometasomathic hematite crystals are similar to cubs or lenses with strong developed rhomboidal forms, volcanogenetic crystals are platy, while metamorphic and hydrothermal ones could be flaky - specular hematite - Figure 1 (Kostov, 1973).

Hematite crystal is without sectility_but with separation in (0001) and (1011) due to the epitacsial layers of goethite. The energy needed for crystal destruction in different directions is shown in Figure 2.

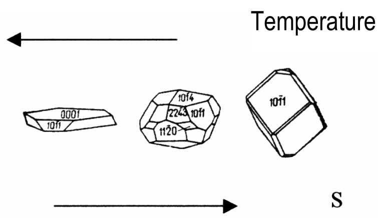


Figure 1. Crystalogenetic trends of hematite

Main usage of MIO type pigments are for anticorrosive coverings. Arrangement the particles parallel to each other results in barrier against access of aggressive fluids, oxygen, UV radiation and different ions to the surface onto which the dye is laid. The barrier effect is illustrated at Figure 3 (Kartner Montanindustrie Ges. mbH, 2001).

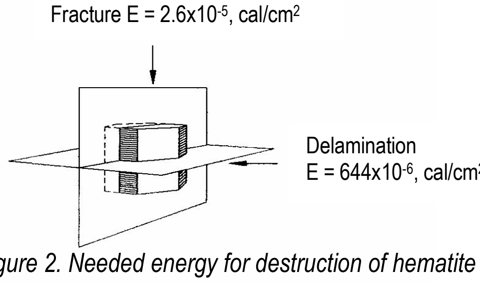


Figure 2. Needed energy for destruction of hematite crystal

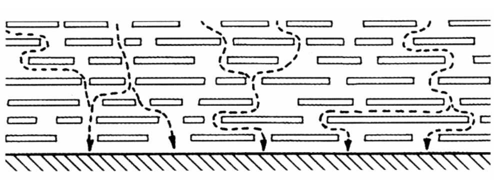


Figure 3. Barrier effect created by MIO particles

Another special feature of the pigment is almost complete absorption of waves with length in the ultraviolet spectrum. UV radiation is dangerous for wood and plastic materials. It has destructive effect onto lignin in the wood and changes the structure of the plastics, which leads to undesired changes in their properties.

At Figure 4 is shown electron microscope picture of cross-section of covering with MIO type pigment.

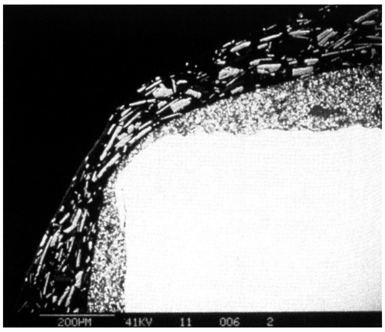


Figure 4. Cross-section of covering of MIO. Electron microscopic picture.

It is known usage of special type pigment - transparent iron oxide (Benbow, 1989). Such pigment has particles with size in range of 0,01 μm (in this size and plate forms they are transparent). Only 2 g/m^2 of this pigment are completely sufficient for 100 % absorption of the UV lights fallen on the surface.

Usage of such type pigment with combination with fine milled mica gives pearl effect of the surface due to the different light-breaking ability of the minerals (Benbow, 1989).

Usage the pigment in the plastic industry is aimed in several directions. Using the painting ability and using the plate forms of the particles - resulting in two subdirections: improving the gasbarrier ability of the plastics and improving its fire resistance.

In spite of continuously increasing application of MIO type pigments the base usage is in anticorrosive coverings of structural constructions including: bridges, pylons, petrol platforms, and other marine outfits as submarines and boats, in fact, everywhere where a good protection from the atmospheric influence and influence of the aggressive medias is needed.

REQUERMANTS TO THE MIO

Several standards were created for the usage of the pigment in the lacquerdye industry. ISO 10601 and ASTM D5532 are valid at the moment. Requirements accordingly the percentage of the flaky particles in the sample of the pigment are defined according ISO 10601. According to this requirement the pigment is categorized. The division is in three grades, where: the first grade should content more than 50 % particles with flaky shape. The other requirements are divided in two categories: essential and conditional. In the group of the essential are:

- Fe_2O_3 content – min 85%;
- Volatile matter at temp. 105°C max. 0,5 %;
- Matter soluble in water max. 0,5 %;
- Granulometric composition:

– + 0,065 mm – 5, 15 and 35 % according to the grade of the pigment;

– + 0.105 mm max 0,1 %.

The defined in the standard conditional requirements, which are not obligatory but are object of agreement between the interested bogies are: pH of the solution, oil absorption and CaO content.

According to the American standard ASTM D5532 the pigments are divided in two grades, where the quality of the first grade is increased in respect of flaky particle content, that should not be bellow 65 % (according the ISO it is 50 %). The other requirements are analogical.

MINING AND PRODUCTION OF MIO

Deposits of quality MIO pigments in the world are limited. MIO is mined in Austria, South Africa, Spain and Morocco in small extends. Austria is the world leader in the production and export of such pigment. Kartner Montanindustrie Ges.mbH mines in Waldenstein deposit in Austria and probably posses 90 % of the world market. Their output is 10 000 t per year while the firm poses capacity to twice the production. The pigment is offered as MIOX trademark and 97 % of it is used in the paint industry. Technology includes – selective mining, separation of the impurities, drying and milling and classification for achievement of the desired from the consumers particle size.

Romero Hermanos SA offers MIO from La Aparacida deposit in Sierra Nevada. G & W Base & Industrial Minerals (PTY) Ltd offers MIO from South Africa.

Attempts for production of synthetic MIO are not achieved yet technological solution adequate to the market requirements. An attempt for production of synthetic MIO is made by Cookson PLS I Magnesium International Copr. They offer product in high purity and high content of Fe_2O_3 under the trademark Laminox.

KREMIKOVTZI AS SOURCE OF MIO

Part of the currently mined iron ore in Kremikovtzi deposit could be used as source for production of iron oxide pigments with wide color range (I. Kuzev, et al. 2001, Atanasov, 1999). More interesting is the fact that specular hematite is found in the deposit. Unfortunately coarse-flaked fraction occurs rarely and it is not restricted in defined areas. Sufficient quantity of fine-flaked fraction could be mined by selective collection.

The coarse-flaked fraction in difference from the fine-flaked does not posses properties to be disintegrated easily. This is the main obstruction for obtaining of MIO from Kremikovtzi deposit. . A special type of treatment that generates predominantly tangential exertion in the milling apparatus is needed. The process of delamination of separate flakes is more probable under such conditions in difference of ordinary process of comminution where the fraction of the particles is more possible.

Practically, the pigment obtained by this method completely fit the conditions of standards defining the quality of pigments type MIO. In the standards is not pointed minimal size or defined granulometric characteristic of the particles. In difference of popular pigment MIO which particles are in range up to 100 μm the maximal size of the particles of the pigment obtained from Kremikovtzi deposit is 10 μm.

METHODOLOGY AND EQUIPMENT

Investigated raw materials is selectively collected from the Kremikovtzi mineral deposit. It includes several types of almost equal in chemical content and with difference in its mineralogy ores. Comparative investigations were made with the following raw materials:

- Coarse-flaked specular hematite;
- Hematite;
- Fine-flaked specular hematite;
- Transition between Hematite and Fine-flaked specular hematite;

The methodology of treatment includes:

- Crushing to 10 mm and 3 mm sizes suitable for the following treatment;
- Vibration treatment – vibration milling and vibration attrition under different conditions:
  - Dry treatment;
  - Wet treatment;
  - Autogenous treatment.
- Sieving or classifying by hydrocyclones according to the desired size.

The investigated technological parameters are:

- Treatment duration;
- The slurry density;
- Filling percentage of the mill;
- Granulometric characteristic of the input;
- Adding of surfactants.

The influence of the different milling medias was investigated. Special working bodies (lenses of tungsten carbide) were used to transform the vibration milling in vibration attrition.

Laboratory vibration devise with volume 350 cm^3 and constant vibration parameters: frequency 24 Hz and amplitude 3,5 mm are used for the purposes of the investigation.

Working medias include rods of different materials – Fe, tungsten carbide, as well as lenses of tungsten carbide for creation of attrition conditions. Lenses of tungsten carbide are shown at Figure 5.

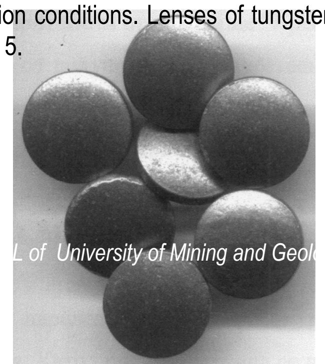


Figure 5. Working media of tungsten carbide

The results were observed by:

- Observation of class (-0,063 mm);
- Defining of the granulometric characteristics by laser devise Analizette 22 made by Fritsch, Germany;
- Optical microscopy with microscope МБИ 15;
- Electron microscopy with microscope Philips 515;
- Image analyze with GALAI CIS 100 carried out in Germany.

Samples of anticorrosive dyes were produced at "Lakprom" research lab Svetovrachane with methodology of the current production applying pigments produced by our technology.

RESULTS AND DISCUSSION

Two methods of treatment were used for obtaining the optimal granulometric characteristic of the input of the vibration attrition stage.

- Consecutive crushing in jaw and roll crusher with outlet of 10 and 3 mm.
- I stage crushing in jaw crusher with outlet of 10 mm followed by II stage vibration treatment with crushing media of steel rod.

Granulometric characteristics of the obtained products are shown at Table 1.

Table 1.

Fraction, mm	Yield, %		
	Hematite	Specular hematite	Fine-flaked specular
+ 1,6	3,0	9,0	2,0
- 1,6 + 1,0	13,0	14,0	10,0
- 1,0 + 0,5	22,0	18,0	20,0
- 0,5 + 0,2	24,0	14,0	23,0
- 0,2 + 0,071	19,0	14,0	22,0
- 0,071	19,0	31,0	23,0
Sum	100,0	100,0	100,0

The second method gives higher yield of fine classes that's way it is preferred in the investigation.

Obtained results from the dry autogenous milling of material with feed size of 14 - 20 mm gives results shown in Table 2.

Table 2.

Treatment duration, min	Yield of observed class – 0,063 mm, %	
	Specular hematite	Hematite
5	11.19	8.33
10	13.05	11.48
20	15.59	13.15
30	15.93	15.19
60	16.10	22.96

Dry autogenous milling of fine-flaked specular hematite has turned out impossible due to generation of agglomerates hampering the process of comminution.

Adding of surfactants does not improve the process even more steppes the process of comminution of hematite and coarse-flaked specular hematite.

Milling by usage of different milling media in dry conditions leads to the following results, shown in Table 3.

Table 3.

Milling media	Yield of observed class – 0,063 mm, %	
	Specular hematite	Hematite
Tungsten carbide lenses	94.50	90.0
Al rod	41.0	28.0
Fe rod	91.0	64.0
WC rod	92.0	70.0

Vibration attrition with milling media of tungsten carbide lenses leads to the biggest yield of observed class of coarse-flaked specular hematite and hematite. Dry vibration attrition of fine-flaked specular hematite has practically turned out impossible due to the fact that fine classes stick to the working bodies and stops the process.

Wet technological process substantially differs from the dry one. Vibration attrition with solid content in the slurry of 71 % leads to 99 % yield of observed class from the coarse-flaked specular hematite, over 67 % for the hematite and 100 % for the fine-flaked specular hematite. With the purpose of comparison treatment with rod working media dives yield of observed class as follows: coarse-flaked specular hematite - 97,5 %, hematite 47 %, fine-flaked specular hematite - 99 %. It seems that the differences in the yields of observed class obtained by vibration milling and vibration attrition is not so high but taking into account the aim of producing particles with flake morphology vibration attrition no doubt has priority (Hristov et al., 2202).

Granulometric characteristics of the products obtained by vibration attrition are shown at Figure 5 and Figure 6.

The sample obtained of fine-flaked specular hematite is in very small size and goes to the zone of unsatisfactory accurateness of the laser devise. That's why it was sent to Germany and analyzed with Image analyzer GALAI CIS 100. Results are shown in Table 4.

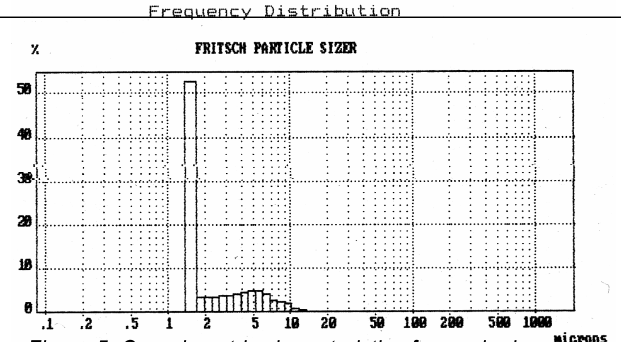


Figure 5. Granulometric characteristic of specular hematite.

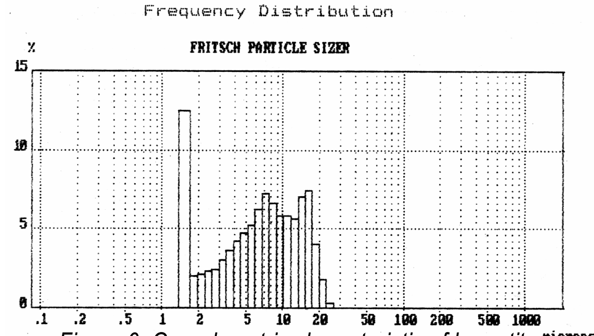


Figure 6. Granulometric characteristic of hematite.

Images from CCD camera were used for the purpose of the analysis. 400 particles were analyzed in tree series of counting. Table 4 represents computer calculated averages of the investigated parameters.

Table 4.

Shape factor	Average Ferret, µm	Min Ferret, µm	Max Ferret, µm	Aspect ratio
0,72	1.18	0.93	1.34	0.43

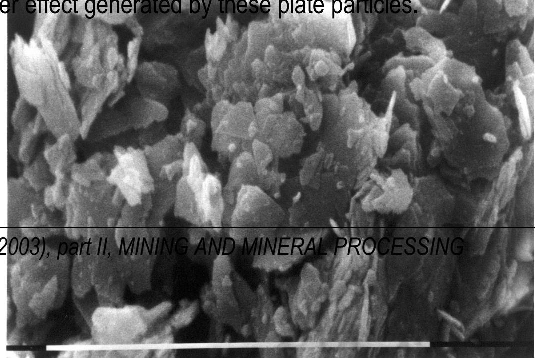
Obtained pigment was analyzed in AES-ICP and Table 5 shows the results.

Table 5.

Contend, %					
SiO_2	Fe_2O_3	TiO_2	Al_2O_3	MnO	CaO
1,92	77,08	<0,01	1,30	0,05	5,33
Contend, %					
MgO	Na_2O	K_2O	P_2O_5	З.П.Н.	H_2O
1,77	3,85	4,66	0,05	<0,05	0,55

The shape of the particles obtained by vibration attrition was observed by scanning electron microscope. A picture is shown at Figure 7.

The analysis of the pigment applied in anticorrosive dye carried out in "Lacprom" shows excellent results. In fact the pigment shows better quality than the pigments used in the current production of the firm. Probably this is due to the flaky shapes of the particles obtained by vibration attrition and barrier effect generated by these plate particles.



Analyzing the obtained results and aiming covering of the requirements to the pigments type MIO we suggest the following technological flowsheet. Figure 8 shows the flowsheet for MIO production from the ore mined in Kremikovtzi mineral deposit.

Figure 7. Particles of fine-flaked specular hematite

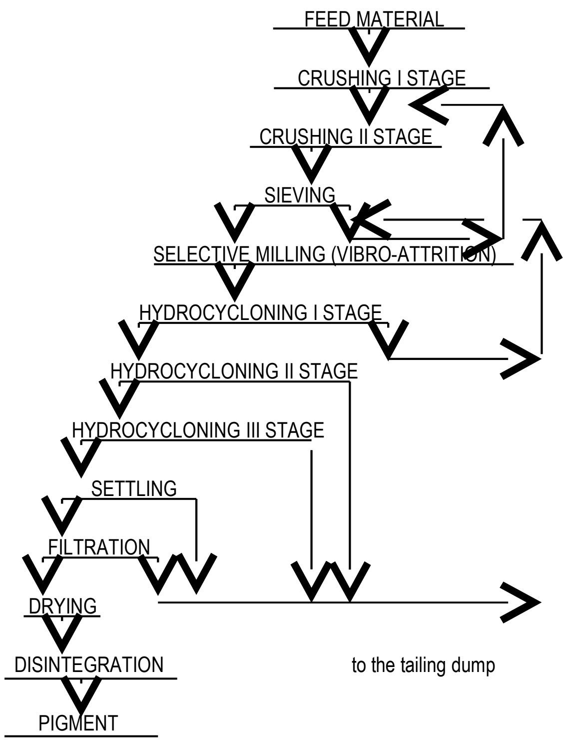


Figure 8 Flowsheet for MIO production

CONCLISION

Characteristic parameters for production of pigment Micro MIO from selective run of mine raw materials from Kremikovtzi mineral deposit were defined by carried out investigation. Technological flowsheet for industrial production are presented. In fact, the obtained pigment fit to the all requirements of standards ISO 10601 and ASTM D 5532. Anticorrosive dye “ПФ – 025” produced by the laboratory obtained pigment fit the recuirements of the technikal sheets (ЛП-ТЦ-ППХ-029 for Fe_2O_3) excluding point - hardness of the film.

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