

Titanium and Zirconium Dioxides



Euro Support BV has been active in the field of catalyst marketing and catalyst toll manufacturing since 1987.

Since 1995 Euro Support BV has been producing custom-made catalysts in the catalyst plant in Litvínov, Czech Republic, formerly owned by Chemopetrol. This plant was started during the 1950s as a strategic operation that would leave the former Czechoslovakia independent from catalyst imports. Through very close cooperation with the Research Institute at the same site, several processes and catalyst systems were developed and operated. Together with the Institute of Chemical Technology in Prague, several high activity/selectivity copper catalysts for selective hydrogenation were developed. Many of these catalysts are still used industrially. In 2001 Eurosupport Manufacturing Czechia, s.r.o. was established, and in 2003 we obtained full ownership of the catalyst plant. One of the main new investments was the building of the catalytic grade TiO_2 production facility. This highly flexible unit produces a large range of catalytic grade titania and zirconia products.



New Titanium and Zirconium Dioxides



New titanium dioxides and zirconium dioxides produced by ESM according to a proprietary technology can be distinguished from similar materials described in literature and/or produced by other companies by the following characteristics:

■ Developed pore structure

The adsorption pore volume ($\text{N}_2, 77\text{K}$) is more than double the size of that of similar products. Also the specific surface area is significantly higher than that of other known products (see data on the next page). The specially developed pore structure is favourable for the use of these types of titanium and zirconium dioxides as carriers for active components in the production of catalysts. In essence, due to the higher surface area and pore volume, the amount of active material which can be supported on these carriers is higher than on known similar products.

■ Increased thermal stability after thermal treatment in the range of $700\text{-}1000^\circ\text{C}$.

■ No binder required for the forming into different shapes, such as tablets and extrudates.

Developed and produced
by Euro Support Manufacturing.

Titanium Dioxides

Titanium dioxide is available in the form of the following MIRKAT Product Families:

■ MIRKAT 200 Series

Mixed anatase and amorphous titania phases with moderate pore volume and a sulfur content calculated as elemental sulfur in the range 0.15 - 0.40 wt%.

■ MIRKAT 300 Series

Mixed anatase and amorphous titania phases with a higher pore volume. The sulfur content calculated as elemental sulfur is in the range 0.12 - 0.30 wt%.

■ MIRKAT 400 Series

Higher pore volume titania in mixed anatase and amorphous phases with enhanced thermal stability. The sulfur content calculated as elemental sulfur is in the range 0.10 - 0.12 wt%.

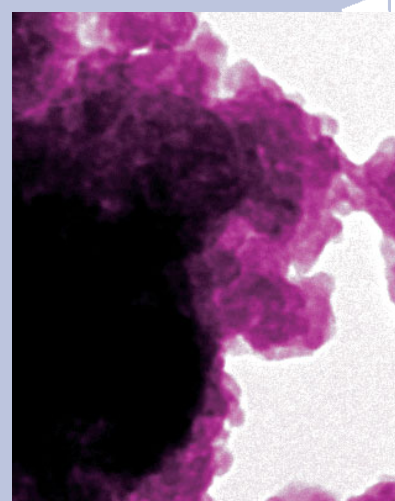
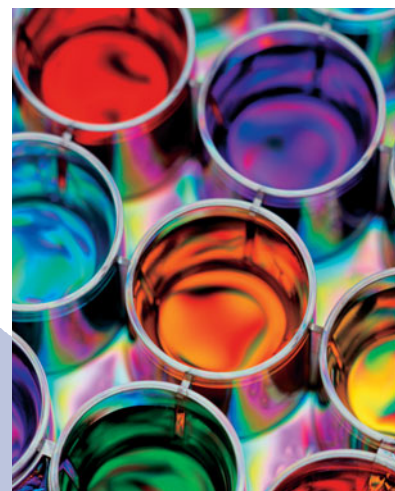
■ MIRKAT 500 Series (low-sulfur anatase)

Titania consisting of a primary anatase phase (not less than 90%). The sulfur content calculated as elemental sulfur is in the range of 0-200 ppmw.

■ MIRKAT 600 Series (stabilized, low-sulfur anatase)

Anatase phase titania with an impurity of amorphous titania, having a high surface area and pore volume, enhanced thermal stability and a sulfur content calculated as elemental sulfur in the range of 15-40 ppmw.

MIRKAT Series 200-500 are being produced on a commercial scale. MIRKAT Series 600 are being produced at pilot plant scale. Additional information on the properties of the above series, which are produced in the form of wet cakes, dry cakes, and granulated product, is given on the next page.



Wet Cakes	Surface Area* (m ² /g)	Pore Volume* (cm ³ /g)
MIRKAT 210	270-300	0.25-0.30
MIRKAT 310	200-350	0.55-0.70
MIRKAT 410	200-350	0.55-0.70
MIRKAT 510	70-170	0.27-0.55
MIRKAT 610	110-190	0.35-0.65

*Analyses are made on samples dried at 150°C, the ranges correspond to different versions of the same type.

Dry cakes

MIRKAT 211, MIRKAT 311, MIRKAT 411, MIRKAT 511, MIRKAT 611 have the same phase composition, physical properties and amount of impurities of sulfur as indicated above for the corresponding families of wet cakes. Compared to competitive titania products, the porosity of MIRKAT products is significantly higher. In the table below a comparison between MIRKAT 411 and a high porosity titania as described in the open literature is given.

Dry Cakes	MIRKAT 411	Literature
Surface area (m ² /g)	200	121
Adsorption pore volume (cm ³ /g)	0.63	0.39
Pore volume (pores of 100 to 200 Å)	0.20	0.20
Pore volume (pores >200 Å)	0.30	0.03

Formed Titanium Dioxides

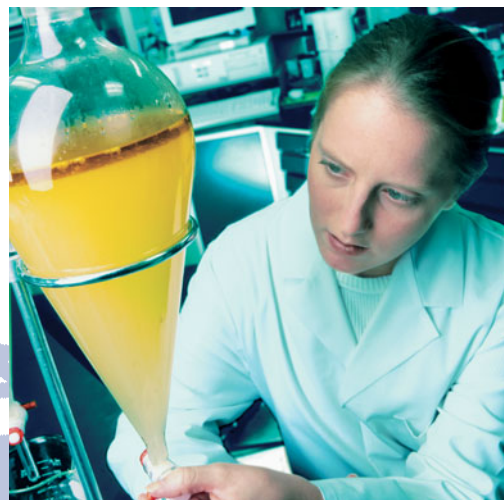
The MIRKAT products can be shaped into different forms, such as tablets and extrudates, without the use of a binder. Tablets of e.g. MIRKAT 435T are characterized by a surface area in the range of 190-230 m²/g, an adsorption pore volume in the range of 0.55-0.65 cm³/g and a loss on ignition of about 5%.

Since the MIRKAT tablets are characterized by a significantly more developed pore structure, MIRKAT 435T is characterized by a relatively low bulk density in the range of 700-750 kg/m³ in comparison with 980-1000 kg/m³ for other known formed titanium dioxides. The crushing strength, in the range 12-20 kg_f, is high enough for use in commercial reactors.

ESM can also produce titania in the form of rings with an outer diameter and a height 5 mm and a diameter of the opening of 2 mm. Since 2003, ESM has been producing titania in the form of tablets destined for use as Claus catalyst. It is being sold under the name S-7001, and more than 25 Claus units worldwide are now using this catalyst.

Zirconium Dioxides

Zirconium dioxide, MIRKAT series Zr-10, is currently produced on a pilot plant scale in the form of wet cake (MIRKAT Zr-11), dry cake (MIRKAT Zr-12) or tablets (MIRKAT Zr-13). The commercial production of these MIRKAT Zr products is in the stage of preparation. The zirconia products are characterized by a developed pore structure and an enhanced thermal stability.



■ MIRKAT Zr-11

Is an amorphous zirconium dioxide being produced in the form of wet cake. Its structural indicators, being determined after drying, are the same as for corresponding dry cake MIRKAT Zr-12.

■ MIRKAT Zr-12

Is a dry amorphous zirconium dioxide with a surface area of approximately of 450 m²/g and a pore volume of about 0.7 cm³/g. An indication of the thermal stability of MIRKAT Zr-12 is illustrated by the following data:

Temperature of Calcination, °C	Surface Area, m ² /g	Pore Volume, cm ³ /g
400	300	0.6
700	150	0.5
1000	60	0.2

■ MIRKAT Zr-12

Is a zirconium dioxide calcined at 700°C comprising of about 75% tetragonal phase, with a balance of amorphous zirconia. After calcination at 1000°C, MIRKAT Zr-12 is totally crystalline with about 65-70% in the tetragonal phase and about 30-35% in the monoclinic phase. This means that even after total crystallization, this type of zirconia still has a significant surface area and pore volume.

■ MIRKAT Zr-13

Zirconia tablets (5 x 5 mm) with a surface area in the range of 250-350 m²/g, an adsorption pore volume in the range of 0.45-0.55 cm³/g, a bulk density in the range of 750-820 kg/m³, a loss on ignition at the level of 5%, and a crushing strength, measured on the face of tablets, in the range of 12 -18 kg_f.



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