

MINERAL FLAKY FILLER FOR COMPOSITES

Technical Field

This invention relates to dispersible flaky
05 materials of uncertain chemical composition, which can be
prepared from the minerals containing lower oxides of
iron (preferably basalt, wind-blown sands, etc.) by
melting the minerals, breaking-up the melt to produce
vitreous hard flakes followed by a chemical modification
10 and incomplete crystallization of the flaky material by
thermochemical treatment in an oxidizing atmosphere.

It is well established that such flakes can be used
as reactive fillers for various composites (preferably
polymerizable composites) in preparing protective and
15 both protective and ornamental coatings featuring high
weather- and water resistance (in protecting metal tanks,
bridges, offshore drilling platforms, etc.) and/or
abrasion resistance (e.g. sludge lines).

Background Art

20 As the description of the technical field suggests,
the fillers of the type described are in great demand.

Accordingly, such fillers must satisfy a number of
requirements that are getting more exact and are not
easily combinable. These fillers are desirable to be:

25 as reactive as possible, the property being
determined from at least the surface area and preferably
by the presence of the active centers over the surface of
such flakes. The active centers constitute a contributory
factor in polymerization of oligomeric binders and in
30 establishing chemical interconnection between macro-
molecules and inorganic components;

as mechanically strong as possible thus providing an
appreciable reinforcement in prepared composites even
with low concentrations of the flaky fillers;

35 as chemically stable as possible (specifically
corrosion resistant) to ease up storage and the use of
the flakes in preparing many types of composites which
usually contain corrosive ingredients while in a green

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state;

commercially available to a variety of customers as a result of large-scale production and low cost.

These requirements taken separately are not too difficult to meet.

US Patent No. 4,363,889 for one discloses a commercially available and somewhat reactive filler for polymerizable composites, prepared as glass flakes of a thickness ranging from 0.5 to 5.0 μm and from 100 to 400 μm in diameter or as a mixture of 10 to 70 parts by weight of such flakes and from 10 to 150 parts by weight of flaky metallic pigments.

Glass flakes are extremely breakable and feature low surface reactivity unless subjected to an additional treatment (e.g. vacuum metallization), while metallic flakes of highly developed surface area are not corrosion stable.

Also known in the art are flaky fillers such as micaceous iron oxide pigments (E.Carter, "Micaceous iron oxide pigments in high performance coatings", *Polymer Paint Colour Journal*, 1986, vol.176, No.4164, pp.226, 228, 230, 232, 234). Compared to glass flakes, they are more durable and chemically stable.

However, such fillers are costly, that is why their use is advisable in applying protective coatings only to such articles and structures where the costs of failure are substantially higher than those of protecting arrangements.

It is, therefore, believed that one of the most preferable ways of providing flaky fillers intended mainly for use in polymer composites is to use flakes produced from natural minerals.

And the present inventor has been involved as a joint originator in developing a technological package including:

a process for the production of finely-dispersed flakes (USSR Pat. No. 1,831,856),

an apparatus for producing finely-dispersed flakes

(USSR Pat. No. 1,823,293).

a method of heat treatment of finely-dispersed flakes and an apparatus for carrying out the method (RU Pat. No. 2,036,748).

05 USSR Pat. No. 1,831,856 discloses a mineral flaky filler produced by melting basalt and dispersing the melt to produce ellipsoidal flakes. Microscopically analyzed for their shape and dimensions, the flakes are characterized, in terms of the ratio between the minor
10 and the major axes of an ellipse, by a distortion from the circular shape within 0.80 and 0.95.

Such flakes remain in the vitreous state and are chemically unstable specifically due to the presence of lower oxides of iron inherent in basalt (and wind-blown
15 sands) used as a raw material. These flakes have low chemical activity as well.

USSR Pat. No. 1,823,293 teaches the manufacture of a mineral flaky filler by substantially the same process and this filler compared with the above-described one is
20 more acceptable as regards its particle size, namely, it contains up to 99% of flakes of substantially identical form and size. However, these flakes again remain in the vitreous state and are chemically unstable, and have low chemical activity.

25 These disadvantages are noticeably eliminated in the mineral flaky filler bearing closely on the invention and disclosed in RU Pat. No. 2,036,748.

This filler is produced by melting a starting mineral (basalt), shaping hard vitreous flaky particles
30 from the melt and by subjecting such particles to thermochemical treatment in an oxidizing atmosphere until a substantially crystal structure is developed. The thermochemical treatment includes heating vitreous particles at the rate of 40 to 190°C/min to a temperature
35 of 600 to 950°C and simultaneously air blowing for 5 to 30 min followed by induced cooling at the rate of at least 950°C/min. The mineral flaky filler treated as above contains substantially no FeO and exhibits high (at least

3 g/cm³) density which is higher than that of vitreous particles by the factor 1.5, higher percentage (up to 53% by weight) of a crystal phase (hereinafter "crystallinity") and noticeable amounts of chemically
05 active paramagnetic centers (hereinafter PMC).

These advantages have provided for an appreciable improvement in the properties of polymerizable composites reinforced with the described mineral flakes and of protective and ornamental coatings produced therefrom
10 (Vesselovsky R.A., V.V.Yefanova, I.P.Petukhov, "Study of physical, chemical, thermodynamic and mechanical properties of interface layers in cross-linked polymers", *Mechanics of Composites*, 1994, vol.30, No.5, pp.3-11; in Russian - Веселовский Р.А., Ефанова В.В., Петухов И.П.
15 Исследование физико-химических, термодинамических и механических свойств граничных слоёв сетчатых полимеров//Механика композитных материалов, 1994, т.30, №5, с.3-11).

Subsequently, it was however found that this filler has no more than 6×10^{19} spin/cm³ of PMC that are active
20 in the process of polymerizing mono- and oligomers (V.V. Yefanova, "Study of the properties of a new activated basalt filler for coating applications", *Ecotechnology and Saving of Resources*, 1993, No.5, pp.67-72; in Russian- Ефанова В.В. Исследование свойств нового активиро-
25 рованного базальтового наполнителя для покрытий//Экотехнологии и ресурсосбережение, 1993, №5, с.67-72). To put it otherwise, the cristallinity mentioned above and chemical activity of the prior art filler are not in balance.

30 Moreover, the present inventor's unpublished experimental findings have proved that the quest for higher cristallinity of the mineral flaky filler is not justified on account of process efficiency as well. For example, the flakes subjected to thermochemical treatment
35 for 30 minutes at temperatures close to the smallest value of the indicated temperature range, i.e. slightly higher than 600°C, show neither detectable cristallinity nor a detectable increase in chemical activity, while an

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increase in the treatment time over 30 min results in a decrease in the product output. A change-over to a relatively short-run (about 5 to 10 min) thermochemical treatment at about 900°C or still higher has been
05 surprisingly found open to uncontrolled revitrification and a decrease in the chemical activity of the particles to be more readily perceived the higher are both the temperature of heating the particles and the rate of cooling the heat-treated particles. And finally, the rate
10 of heating vitrified particles, prior to exposure thereof to a gaseous oxidant such as air, has appeared to virtually have no effect on the progress and result of the treatment. Consequently, use of additional process instrumentation will unjustifiably increase the cost of
15 the end product.

Disclosure of Invention

Therefore, the technical problem underlying the present invention is to provide a mineral flaky filler for composites wherein, by way of improving operating
20 conditions of the thermochemical treatment of the vitreous particles and subsequent cooling thereof, cristallinity and chemical activity would be significantly closer to balance, compared with the prior-art fillers, could be commercially available and,
25 as used in polymerizable composites, would provide for more durable protective and ornamental or abrasion-resistant coatings.

To this end the invention consists in a mineral flaky filler for composites, produced by melting a
30 starting mineral, shaping hard flaky vitreous particles from the melt, and subjecting such particles to thermochemical treatment in an oxidizing atmosphere until a crystal phase is developed, according to the invention at the step of the thermochemical treatment the flaky
35 particles were treated at a temperature range of 680 to 850°C until at least 12% by weight of the crystal phase and at least 7×10^{19} spin/cm³ of reactive PMC are developed, and followed by air cooling.

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The filler thus produced is mechanically strong due to an adequate degree of crystallization and, owing to the congruity of the crystallinity with the chemical activity, it can be used as a highly effective means of upgrading the quality of mainly thick (>1, and typically >3 mm) protective, ornamental, and abrasion-resistant coatings by the use of preferably such binders that are produced under polymerization of mono- and/or oligomers.

It should be mentioned here that production costs were reduced due to a reduction in an investment in the heating, cooling, and control equipment as well as in the costs of power for the thermochemical treatment and for preparing and feeding the coolant. The end product is therefore commercially more readily available.

The mineral flaky filler of the invention is further characterized by containing at least 30% of particles having a mean size of about 100 μm across to the total amount of the particles and at least 14×10^{19} spin/ cm^3 of the PMC to thereby enable such filler to be preferred for use with polymerizable composites.

Best Mode for Carrying out the Invention

The invention is further explained by way of general description and specific data of the experimentation on the method of producing a mineral flaky filler for polymerizable composites, including the values of physical and chemical properties obtained, examples of how the filler is used in polymerizable composites for application as protective coatings, and results of comparative tests on the composites for applying such coatings.

Generally, the method of producing the mineral flaky filler of the invention comprises the steps of:

(1) obtaining hard vitreous particles (usually as flakes) by:

crushing selected mineral to sizes suitable for charging a melting furnace,

heating the charge to obtain a thin melt (specifically, to a temperature of 1400-1500°C for basalt

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and above 1500°C for wind-blown sands),

breaking up a stream of the melt flowing through a heated die into vitreous particles as by a whirler and/or an airstream);

05 (2) thermochemical treatment of the vitreous particles from step (1) in an oxidizing atmosphere (preferably in air) at temperatures from 680 to 850°C (preferably 680-780°C) until an incomplete crystallization, i.e. at least 12% by weight of the
10 crystal phase, and at least 7×10^{19} spin/cm³ of reactive PMC are developed, and followed by air cooling; and, optionally,

(3) mechanical treatment of the particles, e.g. fragmentation and separation according to size, until a
15 mineral flaky filler containing at least 30% of particles having a mean size of about 100 um across to the total amount of the particles and at least 14×10^{19} spin/cm³ of reactive PMC are obtained.

In the production of hard vitreous flakes, use was
20 made of basalt containing about 10% FeO from the Kostopol deposits (Ukraine). The crushed stone of 5 to 40 mm in size was melted in a modified melting furnace similar to a quartz-glass furnace, in which heat is supplied by gas burners. The melt was heated to a temperature of
25 1400-1450°C to be extruded through a heated die of heat-resistant steel in a stream of 8 to 10 mm in diameter. The stream of the melt was broken up in a stream of cooling air by a whirler generally heated to about 1300°C.

30 The flakes obtained were colored gray, about 3 um thick and from 25 um to predominantly 3 mm in size across. The flakes were carefully (to avoid breaking up or compacting) poured over underpans of heat-resistant steel in loose layers from 80 to 100 mm thick, placed into
35 a muffle furnace, and subjected to thermochemical treatment in air at successive temperatures of 660, 680, 750, 850, and 875°C for 90, 60, 30, 20, and 15 minutes, respectively, and then removed from the furnace and

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cooled to room temperature in air.

Samples of the flakes treated at above temperatures were analysed for crystallinity and the PMC by conventional methods.

05 Crystallinity X was defined by the formula

$$X = \frac{d_{tp} - d_{vp}}{d_{cp} - d_{vb}} * 100\%$$

10 where d_{tp} is the density of the particles after treatment,
 d_{vp} is the density of the vitreous particles,
 d_{cp} is the density of the crystal phase,
 d_{vb} is the density of the vitreous body of the particles,

substituting density values defined in xylene into the
 15 formula (G.A.Rashin, N.A.Polkovoi "Certain physico-technical properties of stoneware defined", *Glass and Ceramics*, No.10, 1963, pp.11-14 - in Russian: Рашин Г.А., Полковой Н.А. "Определение некоторых физико-технических свойств каменного литья" в журнале "Стекло и кера-
 20 мика", 1963, №10, с.11-14).

The PMC were counted from electron paramagnetic resonance (EPR) spectra in a mineral filler and diphenylpicrylhydrazine, the latter being a reference substance ("Electron Paramagnetic Resonance" *An Abridged Chemical*
 25 *Encyclopedia*, V, Moscow: Soviet Encyclopedia, pp.961-968 - in Russian: статья "Электронный парамагнитный резонанс" в "Краткой химической энциклопедии", т.5, М: Изд-во "Советская энциклопедия", с.961-968). The EPR-spectra were obtained from the model E/x-2547 radio spectrometer
 30 commercially available from RADIOPAN (Poland).

The analysis findings are summarized in Table 1.

Table 1

CRYSTALLINITY AND PARAMAGNETIC CENTERS
 VS. TREATMENT TEMPERATURE

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Indicators*	Treatment temperatures, °C				
	660	680	750	850	875
Crystallinity, % by wt.	5.8	14.8	35.2	52.3	49.8
PMC, 10^{19} spin/cm ³	5.8	16	18	19	17

*Note: the respective indicators would constitute 0.0% and $<2.0 \times 10^{19}$ spin/cm³ for vitreous particles prior to the thermochemical treatment and 51.5% and about 6.0×10^{19} spin/cm³ for prior-art particles after thermochemical treatment at 900°C, when essentially all FeO has changed to Fe₂O₃.

As will be seen from Table 1, thermochemical treatment of the vitreous particles at temperatures below 680°C is not practicable since both crystallinity and PMC increase but significantly, nor it is practicable at temperatures above 850°C because crystallinity and PMC begin, though insignificantly, to be adversely affected.

Following thermochemical treatment, the mineral flaky filler was crushed and separated according to the particle size to thereby enhance reactivity of the filler. The experiments were performed on the particles treated at 750°C. Samples containing various proportions of particles with a mean size of about 100 um across were prepared and the number of PMC was determined. The results of the experiments are shown in Table 2.

Table 2

PARAMAGNETIC CENTERS
VS. MEAN PARTICLE SIZE ACROSS IN SAMPLES

25	Particles with mean size across <100 um, %						
	5.0	10.0	20.0	30.0	40.0	80.0	
PMC, 10^{19} spin/cm ³	90	210	280	370	560	630	

To assess the effect of the mineral flaky filler of the invention on the physicomachanical properties of polymerizable composites, standard samples were prepared. These were used in determining the adhesive strength (measured as a force required to separate a steel mushroom-like piece from the coating applied to a support also made of steel), the compressive strength, the tensile strength, the modulus of elasticity in lateral flexure, and the impact strength per unit area. Similar samples of the prior art filler were also prepared and used in concurrent tests (the methods and equipment for

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running such tests are well known to those skilled in the art).

In the above tests, the filler of the invention (hereinafter referred IF) was that as prepared by the thermochemical treatment at 680°C prior to crushing and classification and therefore having the lowest crystallinity and PMC counts, while the prior art filler (hereinafter referred PF) was prepared at 900°C and had crystallinity and the PMC counts close to maximum. A relatively simple mixture of acrylic monomers containing polymeric additives and an initiator of polymerization, which are listed in the left column of Table 3, were used as a binder for experimental cold polymerizable composites.

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Table 3

COMPOSITION OF EXPERIMENTAL POLYMERIZABLE COMPOSITES

	Ingredients	Applicable standards	Amount,
		or specifications	parts by wt.
20	Methyl methacrylate	GOST 20370-74	100
	Polybutyl methacrylate	TU 6-01-358-75	20
	Polyvinyl chloride	OST 6-01-37-88	20
	Polyisocyanate	TU 113-03-29-6-84	15
	Benzoyl peroxide*	GOST 2168-83	10*
25	Dimethyl aniline	GOST 14888-78	3
	IF, or		10
	PF		10

*Note: benzoyl peroxide is used in a paste form as a mixture with dimethyl phtalate in approximate ratio by weight of 1:1.

The ingredients were proportioned, methyl methacrylate, polybutyl methacrylate and polyvinyl chloride premixed, then one of the fillers was introduced, with stirring the mix, polyisocyanate and dimethyl aniline added (again with stirring), and lastly benzoyl peroxide was introduced. After a thorough mixing, the compositions were shaped in a conventional way into as many samples as required to obtain data on the

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physicomechanical properties of the composites, the mean square deviation being $\pm 5\%$.

The findings are summarized in Table 4.

Table 4

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COMPARISON OF SAMPLES TESTED

Properties	Filler	
	IF	PF
Adhesive strength, MPa	42	27
10 Compressive strength, MPa	92.0	72.0
Tensile strength, MPa	14.0	9.2
Modulus of elasticity in		
lateral flexure, MPa	36.4	28.5
Impact strength, kJ/m^2	17.3	14.2

15 As can be seen from Table 4 the mineral flaky filler according to invention is more efficient compared with the prior art filler.

Industrial Applicability

20 The industrial applicability of the mineral flaky filler stems from above-disclosed in connection with both possible large-scale production and wide application.

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C L A I M S

1. A mineral flaky filler for composites, produced by melting a starting mineral, shaping hard flaky vitreous particles from the melt, and subjecting such
05 particles to thermochemical treatment in an oxidizing atmosphere until a crystal phase is developed characterized in that at the step of the thermochemical treatment the flaky particles were treated at a temperature range of 680 to 850°C until at least 12% by
10 weight of the crystal phase and at least 7×10^{19} spin/cm³ of reactive paramagnetic centers were developed, and followed by air cooling.

2. A mineral flaky filler of claim 1 characterized in that it contains at least 30% of particles having a
15 mean size of about 100 μ m across to the total amount of the particles and at least 14×10^{19} spin/cm³ of the paramagnetic centers.

