

PROCESS FOR COVERING SILICAS WITH WAX

The present invention relates to a process for covering silicas with wax and the use of such silicas.

Matting agents for coatings based on wax-impregnated silicas are known and described in DE 10 06 100, DE 15 92 865 and EP 0 922 691, for example. In this case, a wax emulsion is converted with a silica suspension, and, if required, a dispersing agent. The impregnated or covered silica thus obtained must then be dried at some expense and also often still contains the dispersing agent. In addition, binding the wax to the silica is inadequate for many applications.

Another process for coating silica with wax is described in EP 0 442 325. Here, the silica is first impregnated with a polyol, facilitating binding of the hydrophobic wax to the hydrophilic silica. Coatings containing the impregnated silica according to EP 0 442 325 exhibit an undesirably high viscosity. Comparative examples in EP 0 442 325 indicate that silicas not coated with wax or coated with wax without the addition of polyol considerably reduce the viscosity of a coating. This is presumably due to the excessively hydrophilic surface of the silica particles compared to the hydrophobic coatings. In order to counteract this effect, a polyol must be added, thus constituting an additional process step.

A thermal process as disclosed in DE 10 06 100 is known for processing silica gels or silica sols. In this case silica hydrogels are first manufactured, dried and activated in a further step. The dried gel is activated by heating it to around 468 - 538°C and then converted with a molten, microcrystalline wax at 371°C, wherein 15 - 30% by weight of wax, relative to the hydrosol, is used. The very fine hydrosol particles exhibit a mesh-type gel structure with a very large water concentration and can therefore only be covered satisfactorily at the above-described high temperatures or high wax concentrations. The high thermal load prohibits the use of many waxes (change in color); furthermore, a rapid cooling of the silica gel thus covered with wax to below the decomposition temperature of the wax must be ensured.

Covering of silicas is not described in DE 10 06 100.

Silicas and silica gels exhibit different structures on account of the different manufacturing processes. Silicas are manufactured by basic precipitation and exhibit an open particle structure. Water can be removed easily from these open-pored particles. In contrast, silica

gels are obtained by acidic precipitation and have a rather closed structure from which water cannot be removed with ease.

The aim of the present invention was therefore to provide a process for covering silicas with wax, which makes for easy handling and enables good sedimentation stability and dispersibility of the silicas, in coatings, for example, with minimal use of wax.

The object of the present invention is therefore a process for covering silica with wax, wherein such covering is carried out at a temperature above the melting range and below the decomposition temperature of the wax in air.

Covering of the silica is preferably performed simultaneously with pulverizing, for instance in an impact mill. In any case, it is appropriate to mix the constituents wax and silica prior to the covering step in a suitable mixing apparatus, such as an Eirich mixer.

The melting and decomposition ranges of the waxes employed in the process according to the present invention are between 40 and 250°C, preferably between 60 and 200°C, and particularly preferably between 70 and 130°C. The process according to the present invention is preferably carried out at these temperatures. The process can be carried out with suitably pre-heated air or heated inert gases.

Suitable silicas are the precipitated silicas described in the examples. However, corresponding Aerosil grades are also suitable. In the process according to the present invention polyethylene (PE) waxes, Fischer-Tropsch waxes or silicone-based waxes can be used for covering purposes. Covering silica with 2 to 15% by weight of wax, preferably 5 to 10% by weight, relative to the silica, has proved itself in practice.

The silicas covered according to the present invention can be utilized as matting agents for coatings such as alkyd resin or other stoving paints.

General Process Description

Precipitated silica and a coating agent (wax) in a ratio of 3 to 15% by weight are mixed together homogeneously in a mixing apparatus, such as an Eirich mixer. This mixture is milled and classified in a classifier mill (e.g. 50 ZPS or similar) or a jet mill. The milling chamber is heated during milling by spraying in heated air (60 - 160°C), in such a way that at the mill outlet the air still has a temperature of 40 - 140°C. The product is separated off by a

filter or cyclone separator. The product covered with the coating agent exhibits a carbon content of 2 to 18% by weight, preferably 3 to 10% by weight, particularly preferably 3 to 6% by weight. The particle fraction can be adjusted by subsequent classification.

Embodiments

Example 1

Data of the silicas used and of the coating agent used.

Table 1

Silica		Coating agent	
BET [m ² /g]	200	micro powder [μm]	8.5
DBP [g/100g]	230	melting point (DSC) [°C]	110-118
d ₁₀	4.66	melt viscosity at 120°C [mm ² /s]	135-240
d ₅₀	9.11	molar mass (GPC) [g/mol]	approx. 3,500
d ₉₀	23.10	density at 23°C [g/cm ³]	0.940-0.955

The precipitated silica from Table 1 is mixed with 6% by weight of PE wax, as in Table 1. In a variation of the process parameters such as classifier speed and milling speed or milling air, the mixture is milled in a Zirkoplex classifier mill 50 ZPS, manufactured by Alpine, at 120°C exit temperature of the milling air, measured at the mill outlet. The test parameters, the physicochemical data and the coating-technical results obtained in a black stoving paint are itemized in Table 2.

Table 2

Classifier speed	[min ⁻¹]	10,500
Mill speed	[min ⁻¹]	9,500
d ₁₀	[μm]	2.82
d ₅₀	[μm]	5.24
d ₉₀	[μm]	8.91
C content	[%]	3.3
Grindometer value	[μm]	30
Gloss 60°		19.7
Gloss 60° rel. to hours		1.7
Sedimentation		2-

Example 2 - Varying the silica and the coating temperature

A precipitated silica, e.g., Sipernat 50, is intimately mixed with a PE wax, e.g., AF 30 (from BASF), in a ratio of 6 parts wax to 94 parts silica. This mixture is fed into an impact classifier mill (ZPS 50). During milling, the impact classifier mill is operated with preheated milling air. The exit temperature of the milling air from the mill is varied. The milling settings (rotary

speed of classifier wheel and mill) are not critical for the coating of the silica with wax but are selected so that the product has a distribution suitable for the desired flattening efficiency.

Parameters of the silica used

BET surface area [m ² /g]	450	
Mean particle size [μm]	27	(instrument: Coulter LS 230)
Tapped density [g/l]	180	(unsieved)
Loss on drying [%]	6.0	(2h at 105°C)
Loss on ignition [%]	5.0	(2h at 1000°C)
pH	6.0	(5% in water)
DBP absorption [g/100 g]	335.0	

Table 3

Exit temperature	[°C]	120	100	80
Name of wax		AF30	AF30	AF30
d ₁₀	[μm]	4.48	4.63	4.67
d ₅₀	[μm]	8.44	8.88	8.54
d ₉₀	[μm]	13.96	14.63	14.05
C content	[%]	5.48	5.94	5.67
Grindometer value	[μm]	25	30	27
60° gloss rel. to std. ^{**}	[%]	-5.5	1.7	0.8
Sedimentation ^{***}		2	2	5
Wax detachment		none	none	

^{*} Instrument: Coulter LS 230

^{**} Standard: Acematt HK 460, Degussa AG

Example 3 - Varying the wax and/or its softening temperature

The experiment is conducted as described in example 1. Waxes having a softening point lower than that used in example 1 are employed.

Table 4

Wax	Manufacturer	Softening point (°C)
AF 30	BASF	105-112
SL 555	Daniel Products	82-86
Aquabead 916	Micropowders	64-67

Table 5

Name of wax		AF 30	SL 555	Aquabead 916
Exit temperature	[°C]	120	120	120
d ₁₀	[µm]	4.48	4.57	4.58
d ₅₀	[µm]	8.44	8.88	8.98
d ₉₀	[µm]	13.96	14.84	15.29
C content	[%]	5.48	5.31	4.97
Grindometer value	[µm]	25	28	29
60° gloss rel.to std.**	[%]	-5.5	-4.9	-5.5
Sedimentation ***		2	2	2
Wax detachment		none	none	none

Table 6

Name of wax		AF 30	SL 555	Aquabead 916
Exit temperature	[°C]	100	100	100
d ₁₀	[µm]	4.57	4.46	4.13
d ₅₀	[µm]	8.88	8.77	7.76
d ₉₀	[µm]	14.63	13.31	11.83
C content	[%]	5.94	5.69	4.97
Grindometer value	[µm]	30	29	31
60° gloss rel.to std.**	[%]	1.7	0.5	-0.1
Sedimentation ***		2	2	2
Wax detachment		none	none	none

Table 7

Name of wax		AF 30	SL 555	Aquabead 916
Exit temperature	[°C]	80	80	80
d ₁₀	[µm]	4.67	4.18	4.15
d ₅₀	[µm]	8.54	8.17	7.79
d ₉₀	[µm]	14.05	12.56	11.75
C content	[%]	5.67	5.79	4.76
Grindometer value	[µm]	27	27	31
60° gloss rel.to std.**	[%]	0.8	1.1	-1.2
Sedimentation		5	2	2
Wax detachment		-	none	none

Instrument: Coulter LS 230

** Standard: Acematt HK 460, Degussa AG

Analytical methods:

***Sedimentation

About 40 g of flatted paint is introduced into glass bottles, which are screwed shut. The samples are stored in a drying cabinet at $50 \pm 2^\circ\text{C}$ for 10 d.

For assessment, the glass bottles are cooled to room temperature.

To test the nature of the sediment, the glass bottles are inverted and the running of the phase containing flatting agent is observed.

Subsequently, the glass bottles are shaken twice by hand. Where sediment is not observed, the base of the bottle is scratched with a needle. By this means, even paper-thin unwanted deposits are detected.

The nature of the sediment is rated as follows:

Rating	Assessment
1	no separation of paint and flatting agent
2	fairly loose sediment (The sediment runs completely from the base and can be dispersed by inverting the bottle once or twice.)
3	soft sediment (The sediment does not run completely from the base but can be dispersed by shaking a number of times.)
4	soft sediment, difficult to reagitate (The sediment is still soft but has already agglomerated to such an extent that it can no longer be adequately dispersed by shaking.)
5	solid sediment.

Wax detachment

1 g of flatting agent and 35 g of ethoxypropyl acetate are weighed out into a 50 ml wide-necked screw-top flask. The cover is closed and the bottle is shaken by hand. The bottle is conditioned at 50°C overnight.

If, under these conditions, wax becomes detached from the flatting agent, it floats on the solvent and the flatting agent settles on the base.

Where there is no wax detachment, there is only a sediment of flatting agent on the base.

The examples show that the coating of the invention must be carried out at above the melting range of the wax. The terms "melting range" and "softening point" are used synonymously here.

CLAIMS:



1. Process for covering silica with wax, characterized in that covering of the silica is carried out at a temperature above the melting range and below the decomposition temperature of the wax in air.
2. Process as claimed in Claim 1, characterized in that milling is carried out simultaneously with the covering process.
3. Process as claimed in any of Claims 1 or 2, characterized in that covering is carried out at a temperature of 40 to 200°C.
4. Process as claimed in any one of Claims 1 to 3, characterized in that 2 to 15% by weight of wax, relative to the silica, are used.
5. Process as claimed in any one of Claims 1 to 4, characterized in that polyethylene waxes, Fischer-Tropsch waxes or silicone-based waxes are used for covering purposes.
6. Use of the silica covered with wax as claimed in any one of Claims 1 to 5 as matting agents in coatings.