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Pigment Encapsulation by Emulsion Polymerisation, Redespersible in Water

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Summary: Emulsion Polymerization was carried out in the presence of inorganic pigments such as TiO2, black FexOy, yellow FexOy, and red FexOy, and NP 30 as surfactants, and water soluble AZO compounds or KPS as initiator. Monomers with specific hydrogen bonding interaction must be used in the initial steps of polymerisation, methylmethacrylate and vinylacetate being the most convenient. Then a semi continuous feed of a mixture of monomers was carried out in starved conditions. In order to make the covered pigments water-redispersible a mixture of hydrophobic and hydrophilic monomers should be chosen with proper pH conditions. The amount of surfactant has to be chosen so that no agglomeration of the covered pigments take place. The covered pigments were dried upon lyophylisation, then formulation of powder paints was carried out using commercial powder binders and other additives. Good properties of the paints, such as brightness were obtained in that way.

Keywords: Pigments, Encapsulation, Emulsion Polymerisation, Acrylic copolymers, Titanium dioxide, Iron oxide

INTRODUCTION

Both patents [1-5] and open litterature papers [6-13] have been devoted to small particles encapsulation using emulsion polymerisation or related processes. Most often the obtained materials display a hybrid character, because the small particles are inorganic (silica, metal oxides, carbon black, etc ...) which are encapsulated by organic polymers (polystyrene, acrylic polymers, etc ....).

In the paint industry, one of the major problems is the dispersion of the pigments in either organic medium (solvant-based paints) or in aqueous medium (waterborne paints). Due to ecological reasons, this last category of paints is gaining more ane more interest. Encapsulation of the pigments with an organic polymeric coating offers an obvious possibility

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of dispersion in an organic medium. Because emulsion polymerisation is carried out in water medium, it should be a good way for the dispersion of pigments in water medium.

Then several works have already been published in that direction[14-22]. One of the earlier work was done by Carris et al. [14,15,16]. These authors have used a TiO_2 pigment modified with an organotitanate unsaturated coupling agent Such modified pigment have strong bonds both with the pigment, through the alcoxyde group able to react with the surface OH groups of the pigment, and the unsaturated group able to participate in the radical polymerisation as a monomer, or ,possibly as a transfer agent. This work was continued[17,18], through copolymerisation of styrene or Methylmethacrylate (MMA) with the titanate coupling agent, which was followed by conductrimetry. By this way, it was possible to follow and detect the various steps of the process, initiation of the polymerisation , limited floculation etc... the same monomers were used by Haga et al.[19] who have shown the importance of the pH, and other parameters, such as the nature of the initiator ; wh en the pigment and the growing polymer have opposite charges, a thick polymer shell is formed around the pigment particle, which cannot be extracted. They have studied also the thermal properties of that shell. A different approach has been used by the team of Templeton-Knight [20,21]. These authors did carried out the emulsion polymerisation, using ultrasonic stirring, at least during the first steps of the process ; then, the thermal decomposition of the persulfate initiator is strongly accelerated, and the polymerisation rate is also increased ; another effect is the disruption of the TiO_2 aggregates, so resulting in a much better encapsulation. Much more recently, in a series of 3 papers, Erdem et al.[22]have discussed the encapsulation of Titanium dioxide in miniemulsion polymerisation of styrene. They used both hydrophilic and hydrophobic pigments . Both pigment particles have a nominal primary diameter of 29 nm. In the first paper,a series of block-copolymer surfactants were tested, and one of them, polybutene-succinimide pentamine (OLOA 370) was retained and studied in more details. Using this dispersant, very good and stable dispersions were obtained in cyclohexane after sonification of the mixture with SDS as surfactant,which allows a very extensive de-agglomeration of the titanium dioxide particles. The smallest particle size were obtained from hydrophilic pigment (40-45 nm) and 1-2% of OLOA, which is almost totally retained at the particle surface and cannot be desorbed again. The second paper describe the transposition of the study to the styrene miniemulsion, while the third paper deals with the polymerisation. Here hexadecane and a small amount of polystyrene were used as hydrophobe to stabilize the miniemulsion. Density gradient column was used to study the encapsulation efficiency, allowing to estimate the distribution of the number of pigment particles by polymer particle. The maximum encapsulation efficiency was shown to be 83% for TiO_2 and 73% for polystyrene. The largest particle size was 209nm containing up to 22 pigment particles in the case of the hydrophilic particles. The hydrophobic lead to poorer encapsulation, with efficiencies around 60% for both polystyrene and pigment. It seems very difficult to obtain a 100% encapsulation efficiency, due to many causes, such as homogeneous nucleation, some remaining large aggregates of pigment and less than 100% of the droplets nucleated.

In the present paper, we describe a rather simple encapsulation procedure of commercial pigments (white TiO_2,,red, yellow or black iron oxides) based on emulsion polymerisation of acrylic monomers. An important feature of the work was to obtain an hydrophilic enough shell of copolymers, so that, after drying , the pigment can be dispersed again in water, upon gentle stirring. Then it should be considered as a component of powder paints. Indeed the powder paints present definite advantages as compared with the conventionnal water-borne paints, being stored in paper bags, and not needing biocides additives, and being able to support long term storage without ageing problems. Most of the work done about the development of redispersible powder paints has been devoted to the problem of binders[23]. Conventionnal binders, but chiefly those from vinylacetate copolymers, can be used ; theredispersion need to use hydrophilic protecting colloids, mainly polyvinylalcohol. The latter, make easy the coalescence of the binder, and then the particles have to be protected against that effect, and in most cases this is done through addition of charges such as montmorillonite.

In our knowledge much less efforts have been done to develop a redispersible pigment.

EXPERIMENTAL

Materials :The pigments are Titanium dioxide RXL from Tioxide, and iron oxides from Bayer : Red OXR 110 M, Yellow OXJ 915, and Black OXN318 M. They have been characterized by elemental analysis, Infra red spectroscopy, surface titration of OH groups, and particle size distribution by quasielastic light scattering.

The monomers, methylmethacrylate acrylic acid, methacrylic acid and others monomers (from Aldrich) were used as received, as well as the surfactants and initiators, all from Aldrich, except the azo compounds from Wako. Deionized water was used all along the experiments.

Pigment dispersion : The reactor was first filled with deionized water and the the surfactants were added, most often a mixture of Sodium dodecylsulfate (SDS) and ethoxylated nonylphenol (NP 40) with about 40 ethyleneoxide units. Finally the pigment was introduced under vigourous stirring. The dispersions were characterized by their pH and their isoelectric point, using a Zetasizer of Malvern, and finally by their average particle size and their particle size distribution, using either a sedimentometer (Br)ookhaven BL DCP Particle sizer) or a granulometer laser (Coulter LS 130) . The sedimentometer allows to determine the T 50 in the cumulative particle size distribution, which is the size corresponding to 50% of the sedimented weight , while the granulometer shows a differential distribution curve in the range between 0.1 and 800 µm.

Encapsulation through emulsion polymerisation : To the dispersion of pigment a slightly watersoluble monomer , such as methylmethacrylate (MMA) is added is added in amount lower than the limit of solubility. Then the temperature of the reactor is established and a semicontinuous addition of the mixture of monomer is added at a slow rate corresponding to starved conditions. Finally there is a cooking step of 2 hours to eliminate most of the residual monomer. After encapsulation the particle size and size distribution are measured , using the granulometer Coulter LS 130.

Water redispersion : Before redispersion, the product is dried through lyophilisation. The coloured powder obtained in the following conditions : congelation –40°C , sublimation – 30°C, final vacuum drying 40°C. The powder is finally grinded and stored in paper bags . For redispersion, 100g of dried powder are pourred in 400 ml of water and gently stirred to obtain a concentrate pigment paste.

Paint tests : In order to have a good estimate of the pigment dispersion, it is introduced in a varnish formulation given in Table 1.

Table 1. Varnish formulation

The pigment powder18.2 g) is first dispersed in 46.1 g of water containing 0.74 g of an anti-foam agent under stirring 5 min (250 rpm)

Then the following items are added : acrylic resin (mowlith DN 777) 127g, bactericide 0.36g, texanol (coalescence agent) 1.6 g, White spirit (coqlescence agent) 2.4 g, Thickener (viscotex) 2.4 g and ammonia 1g

A final mixing step of 10 minutes is carried out.

.When the dispersion seems good enough with only a few agglomerates, three items are measured : gloss at 60°, gloss at 85° and contrast ratio R.

Further estimate involve some comparison between a reference formulation of external paint and an experimental one containing the encapsulated pigment.

RESULTS AND DISCUSSION

The elemental analysis of the pigments is reported in Table 2, together with the number of surface OH groups. And indication of their acido-basic character (for instance, the ζpotential of the titanium dioxide is -21 at pH 7). The pigment dispersion state is strongly dependent on the surfactant system associated with it, and the best results obtained are shown in Table 3.

Table 2. Pigment analysis

Pigment	Ti%,Si%,Al %	C %	N oh μmol/m^2	Area m^2/g	character
TiO_2 RXL	45.2,4.8,2.3	<0.2	3.5	26	basic
Red,αFe_2O_3		<0.2		14.4	acidic
Yellow $\alpha FeOOH$		<0.2	20.0	20.4	acidic
Black,γFe_2O_3		<0.2	14.9	14.3	acidic

Table 3. Pigment dispersions in water

Pigment	Surfactant system, g	Particle size, nm	Poly.index
TiO_2 RXL	SDS 1.6 – NP40 1	330	1.4
Red,αFe_2O_3	SDS 1.6 – NP40 1	290	1.2
Yellow, $\alpha FeOOH$	SDS 1.6 – NP40 1	1080	1.4
Black,γFe_2O_3	SDS 1.6 – NP 40 1	3500	2

The coloured pigments are more difficult to be dispersed and their particle size remains rather big and polydisperse, except for the red pigment.A typical picture from Scanning Electron Microscope(SEM) is shown in figure 1.

In a first step, the encapsulation of the Titanium dioxide pigment from emulsion polymerisation has been carried out , using methylmethacrylate as monomer only. A variety of initiators have been tested and the bests were found to be Potassium persulfate (KPS) and a watersoluble azo VA86 , $HOCH_2CH_2NHCO\ C(CH_3)_2N{=}N\ C(CH_3)_2CONH\ CH_2CH_2OH$. Both initiators lead to high conversions within five hours before the cooking step.

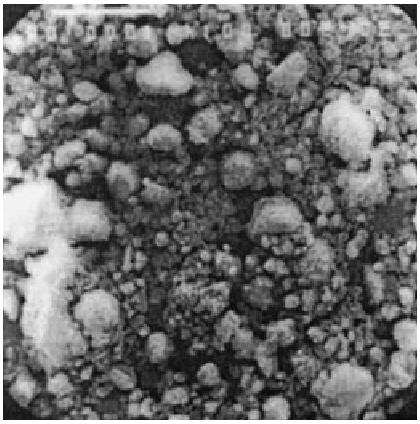

Figure 1. SEM image of Titanium dioxide not yet encapsulated

The amount of MMA added in the semi batch process was calculated in order to cover the pigment particles with a homogeneous shell of 50 nm thick. However, it turns that the particle size increases from 330 to 830 (VA86) or 900 (KPS) nm, and the powder cannot be redispersed. A typical picture from SEM is shown in figure 2.

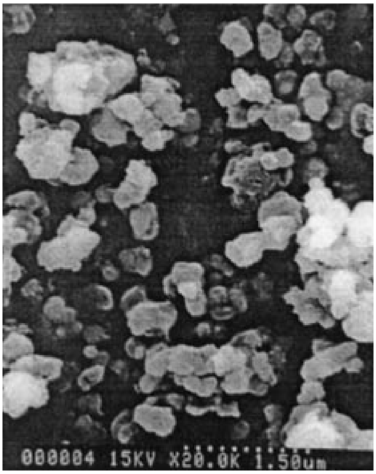

Figure 2. SEM image of Titanium dioxide encapsulated with emulsion copolymerisation of a mixture 3/1 of MMA and MAA, not neutralized

It was decided to add to the MMA a watersoluble monomer. A few methacrylic polyethyleneoxide(PEO) macromonomers were tested first. Promising results, in terms of redispersibility and particle size were obtained when the number of EO units was limited. A variety of watersoluble monomers were tested as well, and the best results have been obtained, using Methacrylic acid or acrylic acids in rather high amounts (25% versus MMA) . Typical data are reported in Table 4.

Table 4. Data of encapsulation of Pigment RXL using carboxylic acid monomers

Comonomer	% evrsus MMA	Varnish Test	Particle size μ	Poly. index
Methacrylic acid	5	A	3.7	1.4
	12.5	RG	2.5	1.1
	25	G	5.1	1.01
Acrylic acid	5	A	6.1	1.2
	12.5	RG	3.8	1.5
	25	RG	3.8	1.1
AHPSulfonate	5	B	0.43	3.8
V pyrolydone	5	B	2.05	1.7

A= acceptable ,B=bad, RG=rather good, G=good
The data of particle size and polydispersity index are obtained after grinding the powder

These products showed still a rather big particle size, even if the distribution is not very large as shown in figure 3.

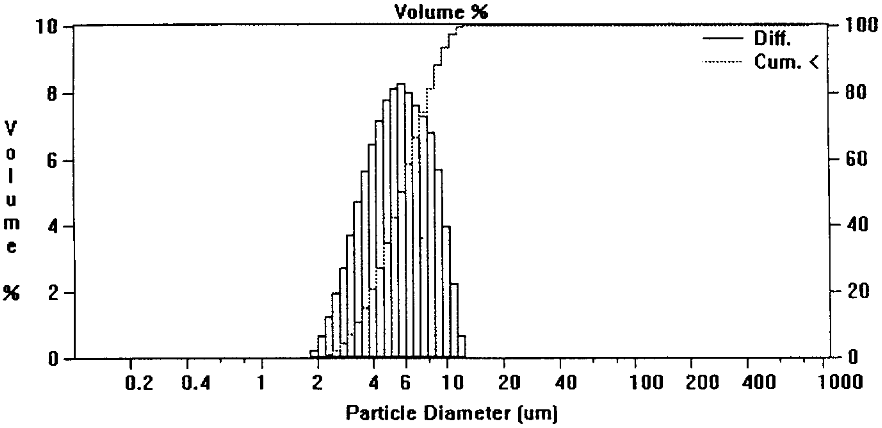

Figure 3.Particle size distribution of Titanium dioxide pigment encapsulated from emulsion copolymerisation of a mixture unneutralized of MMA and MAA (3/1)

More detailed study did show that floculation took place after about 30% conversion. In order to avoid that floculation, it was tempted to neutralized, at least partially , the carboxylic groups, so providing additionnal electrostatic stabilization to improved the stabilization given by the surfactants.Then,it can be seen in figure 4 that either the floculation do not take place or lead to agglomerate which can be destroyed upon grinding.. Corresponding data are reported in Table 5 ; showing results of the test of addition in the varnish formulation.

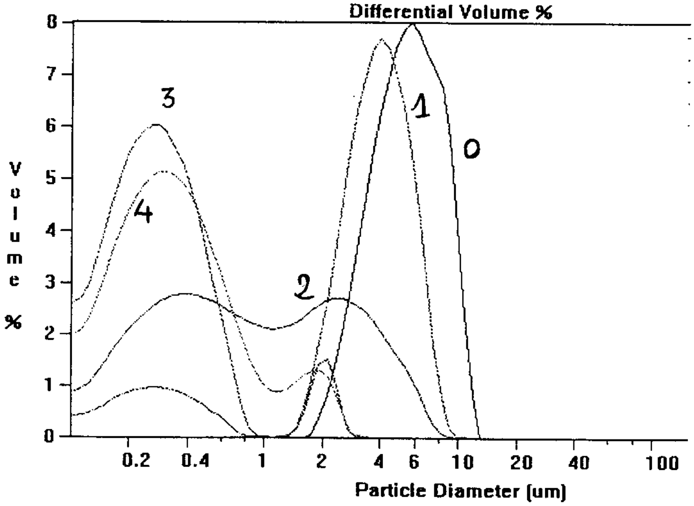

Figure 4. Particle size distribution of Titanium dioxide pigment encapsulated from emulsion copolymerisation of a mixture of MMA and MAA (3/1)neutralized partially through addition of soda

While the data reported in Table 4 indicate the a rather large amount of carboxylic monomer is needed, Methacrylic acir being the best monomer and that the other monomers failed to give acceptable results in terms of paint tests, those reported in table 5 show that partial neutralisation of the acid groups lead to a definite improvement of the properties of the pigment powder in the paint formulations . However, it is clear that there are optimal neutralisation conditions which seemed to correspond to 2 g of added soda .The best quality seems to involve,in terms of gloss and contrast ratio, not the smaller size, but a polydisperse distribution of small size particles with 2 populations

Table 5. Data of encapsulation of Pigment RXL using partilly neutralized methacrylic acid

	%MAA	Soda g	Size μ	P.Index	N pop	V Test	G 60°	G 85°	R
Ref.	30	0	5.5	1.1	1	G	5.9	17.4	82
1	30	1	3.6	1.1	1	G	10.6	55.2	86.2
2	30	2	0.83	1.8	2	VG	26.9	68.5	90.6
3	30	3	0.33	1.5	2	G	15.6	34	85.4
4	30	4	0.28	1.5	1	G	26.6	23.2	83.2
5	30	10	0.52	2.3	2	RG	16.2	22.2	85.5

V.Test = quality of the varnish : G=good, RG=rather good, VG= very good
G 60° = gloss at 60° , G 85°= gloss at 85°, R= contrast ratio
P index = polydispersity index , N pop= number of particle populations

The encapsulated RXL titanium dioxide pigment was used also in paint formulations with a variety of commercial charges with good sucess. A high contrast ratio can be reached with less Titanium, but the abrasion resistance in wet conditions is slightly lower, but still better than powdered pigments recently introduced in the market.

Similar studies have been carried out with coloured pigments with good sucess. Some results with the three coloured pigments mentionned in Table 2 and 3 are reported in Table 6.

Table 6. Data for iron oxides encapsulation

Run	Soda g	Size μ	P index	N pop	V Test	G 60°	G 85°	R
1 Red	0				A	9.9	28.1	99.4
2 Red	4 VA86	0.77	1.3	2	VG	20.1	51.3	99.3
3 Red	4 KPS	1.25	1.4	2	VG	29.8	65.5	99.9
4 Black	4	2.8	1.4	2	VG	26.7	63.7	99.9
5Yellow	10	0.54	1.3	1	A	11.5	12.7	90.5
6Yellow	5	0.44	1.1	1	VG	36.7	62.1	97.6
7 Red	4 V501	2.65	1.2	2	G	25.2	46.1	99.9

All the samples have the same composition : MMA/ MAA = 3/1
P index = polydispersity index , N pop = Number of particle populations
V.Test = quality of the varnish : G=good, RG=rather good, VG= very good, A=acceptable
G 60° = gloss at 60° , G 85°= gloss at 85°, R= contrast ratio

Most of the trials have been very successfull, chiefly concerning contrast ratios, which are maximum in most cases. With the red pigment a cationic initiator lead to poorer results than the more classical initiators. Very good results for paints are obtained even if the particle size is big, as it is in the case of the black pigment ; in this case it seems that the polymerisation process helps to break the agglomerates of the initial dispersion, because, as shown upon comparing the data of Table 3 and 6, the final size is smaller than the initial one. It is possible that this feature can be a general one, where there is an equilibrium between agglomeration and dispersion during the encapsulation process. Such feature is illustrated in figure 5, where one can see the particle distribution corresponding to run 2 where a small population of bigger particles can be observed. Run 5 with the yellow pigment shows again that the best results are not obtained when the degree of neutralisation of the carboxylic groups in the copolymer is too high .

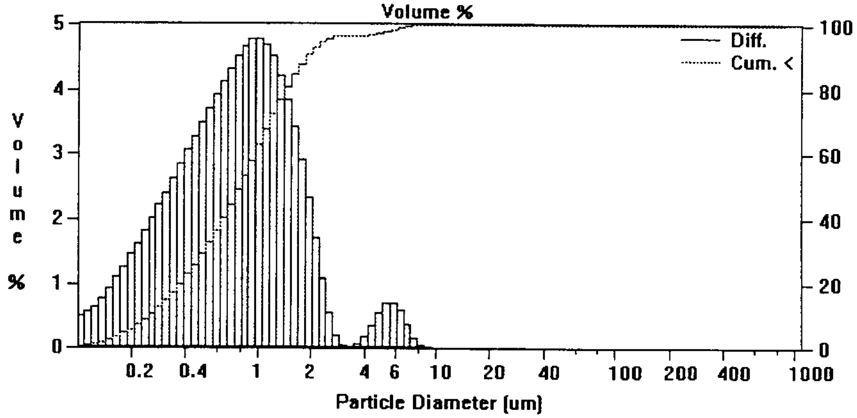

Figure 5.: Particle size distribution of Hematite red pigment encapsulated from emulsion copolymerisation of a mixture of MMA and MAA (3/1) partially neutralized upon addition of 0,1,2,3 or 4 g of soda.

CONCLUSION

Emulsion copolymerisation of MMA associated with a hydrophilic monomer such as MAA carried out in the presence of a mineral pigment (TiO_2 or Iron oxides of various colors) allows to obtain, upon partial neutralization of the carboxylic acid with soda, a pigment dispersion, which can be dried, grinded in powderpowder and then easily redispersed in water. The product can be used as a component of the formulation of a powdered paint, which are known to be a real progress from the ecological point of view, because they can be stored simply in paper bags for long time without biocide components, have no VOC and can be used leaving a minimum of residues which must be destroyed. At variance with other products recently introduced in the market, these powdered pigments affect only hardly the performances of the paints in the presence of humidity.

We think, however that progress should be made chiefly through optimisation of the process, for instance upon better analysis of the particle size distribution during the polymerisation, to obtain the best compromise between the dispersion and the trend of the particles to agglomerate. Another progress should be to extend the encapsulation to the organic pigments, and promising results have be obtained in our laboratory, using miniemulsion polymerisation (ref.24).

Finally, another kind of progress should be to combine, in the same powder both the pigment and the binder. We have begun to work in that direction, and have obtained just a few promising results, but a lot of work is still needed to get success in this connection.

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