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Dispersion of Three Ceramic Powders in a Slurry. The Al_2O_3–AlN–SiC Mixture

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Abstract

This work presents, in a first stage the influence of aluminium nitride (AlN) addition to a well dispersed α-alumina slurry, and in a second stage the influence of silicon carbide (SiC) phase to a Al_2O_3–AlN slurry. We have shown that the acid–basic character of polymer dispersants and powder surface play a major role in the adsorption phenomena of dispersant onto a surface: an acidic polymer will have a better affinity with a basic powder surface than with an acidic surface and vice versa. This study has allowed to determine the dispersion conditions of each powder in an azeotrope medium (methyl ethyl ketone–ethanol) with phosphoric ester (PE) on Al_2O_3 powder and polyvinylpyrrolidone (PVP) on SiC and AlN powders. If, for two components (Al_2O_3–AlN) the best conditions of dispersion lead to a homogeneous material, it is not the same for three-powder mixtures (Al_2O_3–AlN–SiC).

1 Introduction

An homogeneous uniform product can only be obtained if the starting suspension has a high homogeneity and stability. This homogeneity must be preserved during all the processing steps: casting, drying, burning-out, and sintering. This requires a careful selection and an accurate control of the processing additives used in the slurry formulation. In our laboratory 'Céramiques Spéciales' a new material Al_2O_3–AlON–SiC has been developed by reactive sintering between alumina–aluminium nitride[1,2] and silicon carbide, which presents a good capacity for cutting tools.[3] The good dispersion of these three phases in a slurry will contribute to a good homogeneity and a good reactivity between Al_2O_3 and AlN in the sintered material. Many authors have studied systems constituted by only one powder in different media.[4,5] So for binary or ternary ceramics suspensions, the complex particulate interactions that determine the overall processing behaviour are difficult to quantify. The aim of this work will be to review the role of dispersants, focusing on their effects on the slurry behaviour and therefore on the material sintering characteristics.

2 Experimental Procedures

The three powders used were, α-alumina CR 6 (Baïkowski, France) marked A, grade B aluminium nitride (H. C. Starck, Germany) marked N, and the grade B-10 silicon carbide (H. C. Starck, Germany) marked Sß. The slurry of each component has been realised in an azeotropic medium, methyl ethyl ketone (66 vol%) + ethanol (34 vol%). The dispersants used in this study were an anionic polymer: phosphoric ester (CECA, France) marked 1, and a nonionic polymer: polyvinylpyrrolidone (PVP; MW≈40,000; Rhône Poulenc, France) marked 2. The suspensions of alumina and aluminum nitride (60 wt%) have been dispersed using ultrasonics for 3 min, while the silicon carbide slurry (50 wt%) has been only mixed with a magnetic stirrer.

2.1 Rheology

To measure viscosity and rheological behaviour, a Haake Rotovisco RV-12 viscometer fitted with a concentric cylinder measuring head has been used. A small sample (9 cm^3) of the slurry was placed between the walls of the concentric cylinder, and the resistance to rotation of the rotor cylinder was measured in accordance with the rate gradient. For these measurements the shear rate was scanned from zero to 350 s^{-1} in 5 min, after a level of 1 min, the scan is realised from 350 s^{-1} to zero. The temperature was controlled by a thermoregulator circulating water bath and fixed at 17·5°C to minimise the medium evaporation.

2.2 Granulometry

Granulometry measurements have been carried out with a laser system apparatus (LS 130, Coultronics), after a dilution of the slurry droplets in an azeotropic medium (200 cm^3).

2.3 Sedimentation test

The fall of suspension/solution interface characterises the dispersion state and the stability state of a suspension. This has been realised in a graduated tube, after a dilution of the slurry (60 wt %) to 23 wt%.

2.4 Surface charge of particles

The zeta potential (ζ) of particles has been determined by the microelectrophoretic method, using an apparatus with a quartz cell (Pen Kem, Model 501).

2.5 Sample preparation

The slurries were dried in vacuum, then the powder sieved to 200 μm. The samples were pressed by isostatic compression at 400 MPa (Ø≈ 20 mm) to determine green density, and sintered either by pressureless sintering for samples without SiC (1685°C or 1750°C, 1 h) in a nitrogen atmosphere or, for those containing SiC, by hot pressing (1710°C, 40 MPa, 0·5 h) in a nitrogen atmosphere, with 7 g powder mixture.

3 Results

3.1 Alumina–aluminum nitride composite

3.1.1 Alumina–aluminium nitride slurry

A previous viscometry study allowed us to determine the deflocculant concentrations which are 1·1 wt% PE or 0·9 wt% PVP for alumina slurry in azeotropic medium. The 3·12 wt% AlN slurry addition to the alumina slurry has induced the observation of two different rheological behaviours. The suspensions of AlNj type, show a lower viscosity than the A2Nj type slurry (Table 1), the AlN2 slurry presenting the lowest viscosity.

The granulometric curves did not allow differentiation of the four slurry types (Fig. 1). It seems the dilution chosen for these measurements has erased the differences observed in the concentrated suspension.

Table 1. Apparent viscosity of mixtures slurries at 350 s^{-1}

Slurry mixture	*Viscosity (mPa s)*
A1N1	4·6–4·8
A1N2	4·1–4·3
A2N1	6·0–6·2
A2N2	6·0–6·2

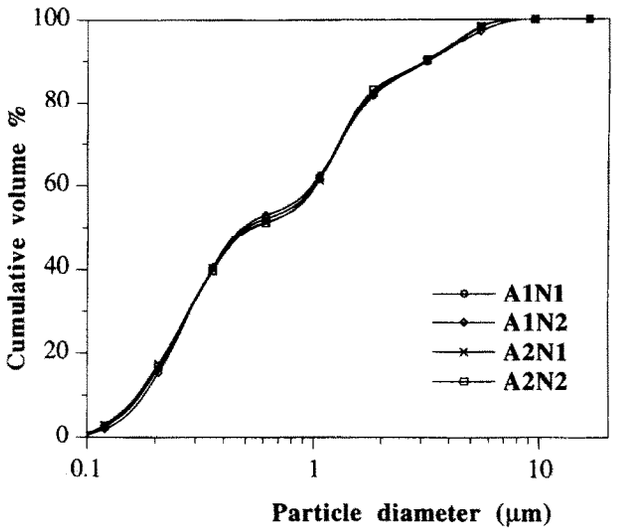


Fig. 1. Granulometric distribution of different slurries.

3.1.2 Sintering results

As observed for the rheological results, we can do the same observation on the mixtures in which alumina has been dispersed by PE which present higher green densification than samples in which alumina has been dispersed by PVP (Table 2).

After sintering, the samples in which aluminum nitride which has been dispersed by PVP in the slurry (AlN2 and A2N2) show a better densification than other samples of AlN1 type. So the mixture realised in suspension did not affect the reactivity between alumina and aluminum nitride because all the samples present the same AlON content, determined by X-ray diffraction.

Figure 2 shows the AlON (white colour) distribution in an alumina matrix. We can observe in A2N1 sample (Fig. 2e) a large porosity; around it no AlON phase is observed. The AlN1 sample (Fig. 2a) shows a large agglomerate of AlON: in the later two cases a bad dispersion during the slurry preparation has led to a bad microstructure of final material. In the AlN2 sample types (Fig. 2b, d), we observe an homogeneity of the AlON phase distribution in the alumina matrix.

3.2 Alumina–aluminum nitride and silicon carbide composite

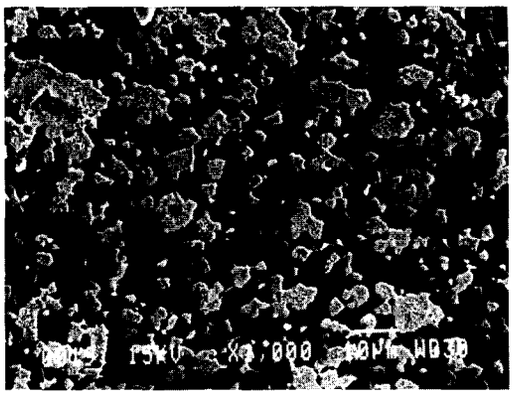
3.2.1 Alumina–aluminium nitride–silicon carbide slurry

Figure 3 shows flow curves of four mixtures, in which Al_2O_3 and AlN are deflocculated by PE or PVP, and SiC powder is deflocculated by PVP only, silicon carbide powder representing 20 wt% of the total powder mass. We can observe two kinds of rheological behaviour. The first corresponds to slurries in which alumina has been dispersed by PVP which show high viscosity and a pseudo-plastic behaviour. The second group of slurries, in which alumina has been dispersed by

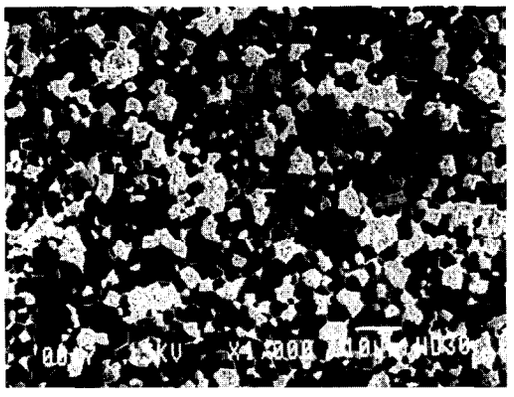
PE, presents a quasi-newtonian behaviour and a lower viscosity. The granulometric distribution curves (Fig. 4) allow observation of the same groups characterised by viscosimetry measurements. The slurries in which alumina is dispersed by PVP present a population about 1·4 μm higher than

Table 2. Green and sintered densification of samples produced from slurries with or without SiC. Mol% AlON represents the AlON content in sintered material

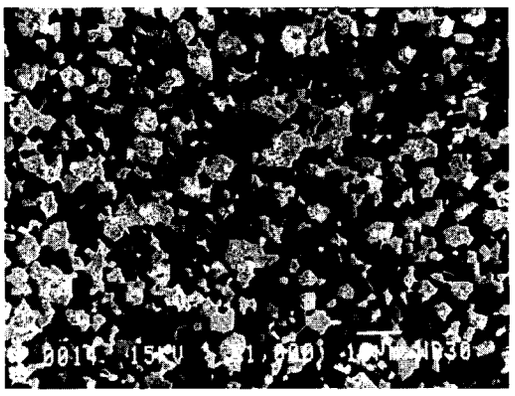
	d_{green} (%)	$d_{sintered}$ (%) (1685°C)	AlON mol%		d_{green} (%)	$d_{sintered}$ (%) (1710°C)	AlON mol%
A1N1	54·5 ± 0·5	95·9	20	A1N1Sß2	58·3	96·8	17
A1N2	54·8 ± 0·4	98·8	20	A1N2Sß2	57·9	97·4	17
A2N1	53·5 ± 0·5	95·1	20	A2N1Sß2	57·2	97·0	17
A2N2	53·8 ± 0·3	98·4	20	A2N2Sß2	56·8	97·4	17



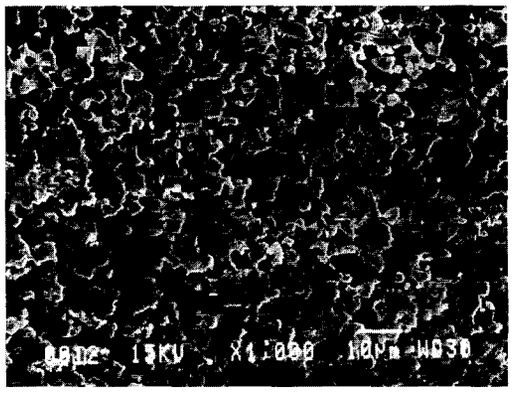
a) **A1N1** —— **10 µm**



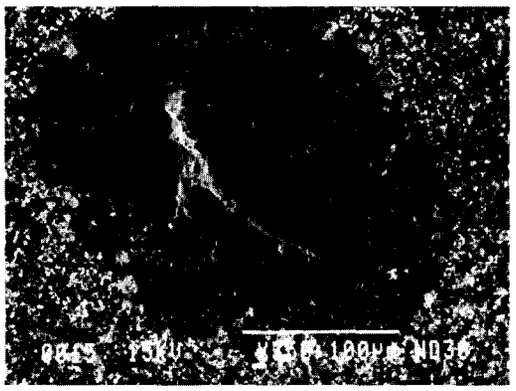
b) **A1N2** —— **10 µm**



c) **A2N1** —— **10 µm**



d) **A2N2** —— **10 µm**



e) **A1N2** —— **100 µm**

Fig. 2. Microstructures of Al_2O_3–AlON composite sintered at 1685°C. (a) AlN1, (b) AlN2, (c) A2N1, (d) A2N2, (e) A2N1 (low magnification).

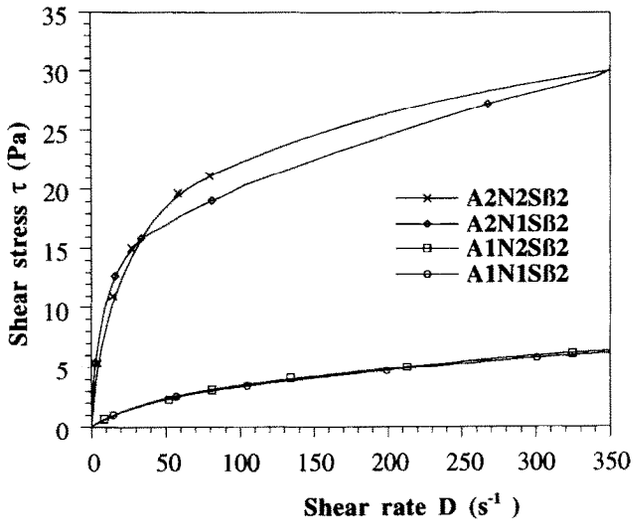


Fig. 3. Flow curves of different slurries.

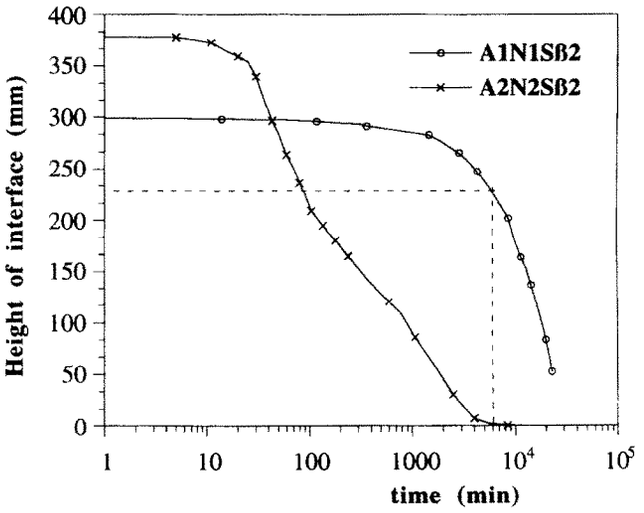


Fig. 5. Fall of suspension/solution interface against time.

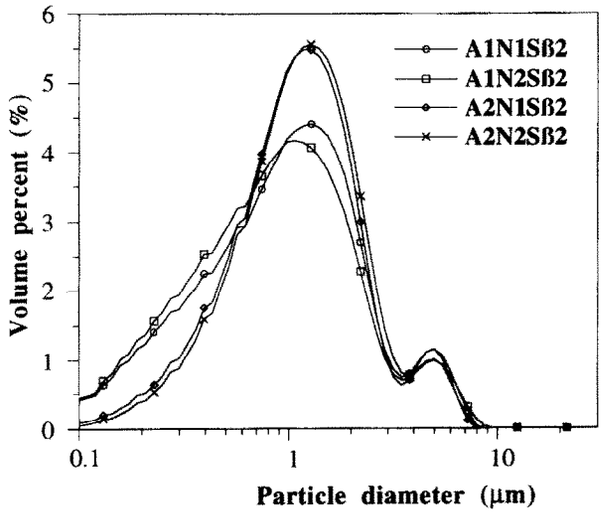


Fig. 4. Particles size distribution of different mixtures.

slurries in which alumina is dispersed by PE. This difference could explain the different behaviours observed in rheological measurements.

The results of sedimentation (Fig. 5) show a long-lasting stability of the slurry in which alumina has been deflocculated by PE, while the slurry in which alumina has been deflocculated by PVP shows a rapid fall of the interface suspension/solution, corresponding to the low stability of this suspension. Moreover, the compactness of sediment shows a higher density of sediment suspension when alumina has been dispersed by PE (40·6%) than when it is dispersed by PVP (18·4%). They suggest that the suspension in which alumina has been dispersed by PVP is less de-agglomerated than one dispersed by PE.

3.2.2 Surface charge and pH measurements in azeotropic medium

These are collected in Table 3. The affinity between the powder surface and the dispersant could be explained by the acid–base character of the dispersant/ surface pair. An acid surface (SiC) has a better affinity with a basic dispersant (PVP), whereas the alumina, which presents a basic surface, has the best affinity with an acid dispersant (PE). For aluminium nitride powder, it seems the PVP provides a slightly better deflocculation than PE.

3.2.3. Sintering results

The results of green and sintered densities collected in Table 2 show the reactivity between alumina and aluminium nitride is not influenced by the dispersion of different phases in suspension, whatever the dispersant/powder combination. We can verify that the green compact of samples which presented low viscosity and high stability (AlNj and AlNjSß2) showed a slightly higher densification than compacts which presented higher viscosity (A2Nj and A2NjSß2).

The samples without SiC show, when aluminium nitride has been dispersed by PVP, a higher densification than when it has been dispersed by PE. In the presence of SiC this difference is weaker. Also in the last case an inhomogeneity has been observed. Actually, when alumina has been dispersed by PE we observe a corona, in which the centre presents a low AlON concentration (white stain) and the exterior presents a higher AlON concentration (Fig. 6 e, f). Attrition milling of the slurries avoids these microstructural inhomogeneities.

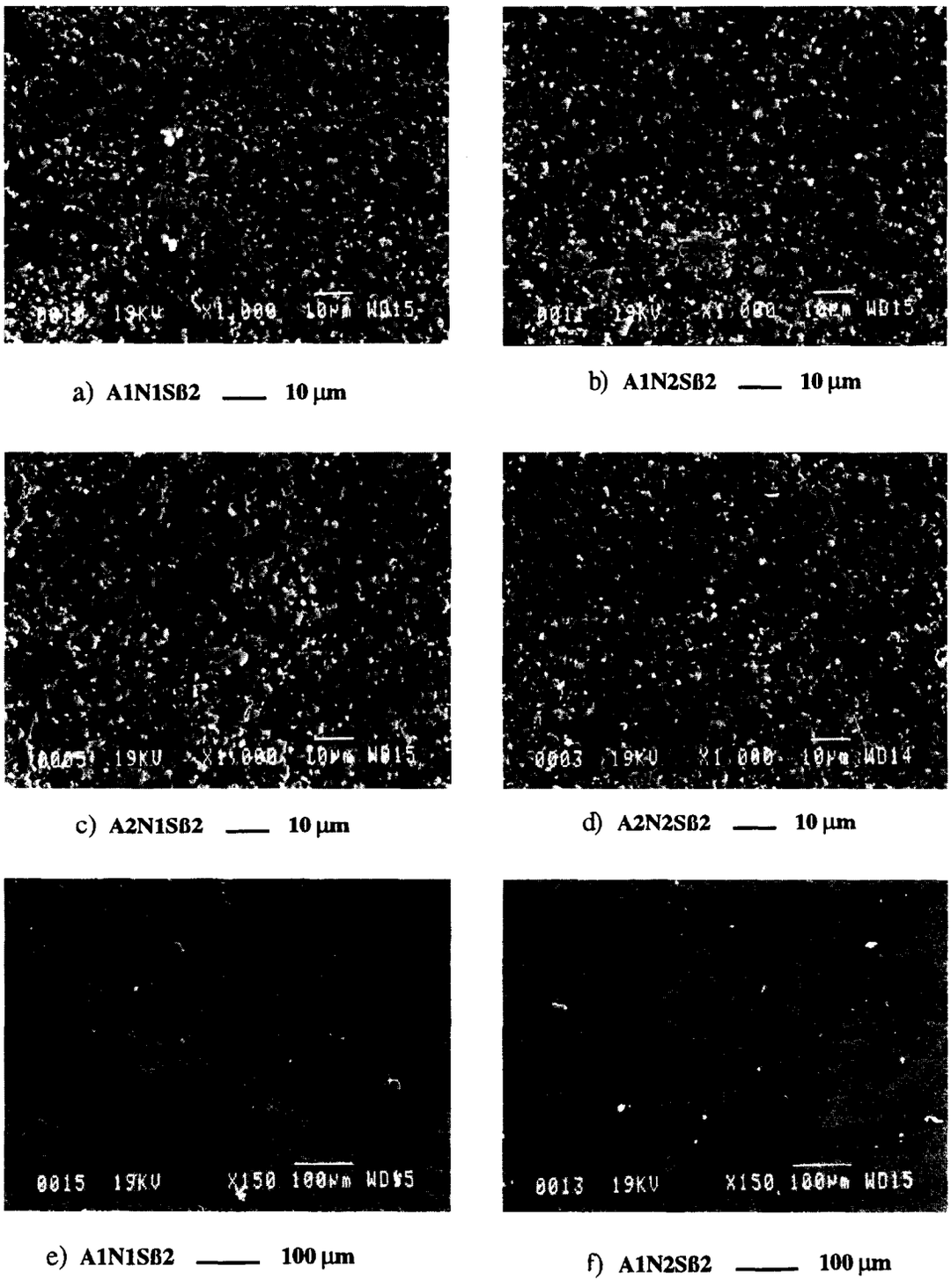
4 Conclusion

This study arrives at three major results:

— *a priori*, the alumina and the aluminium nitride presented the same hydroxyl surface, nevertheless their surfaces do not have the same affinity with these two dispersants. The acid–base character of dispersant and powder surface determine the

Table 3. Zeta potential of particles in azeotrope medium with or without dispersant and pH measurements of this solution

	Al_2O_3		AlN		SiC	
	pH	*Charge ζ (mV)*	*pH*	*Charge ζ (mV)*	*pH*	*Charge ζ (mV)*
Azeotrope	6·2–6·8	/	6·2–6·8	/	6·2–6·8	/
Azeotrope + powder	7·2	–4·0	9·2	+17·5	4·7	–1
Azeotrope + PE	3·4	/	3·4	/	3·4	/
Azeotrope + powder + PE	4·3	+12·5	4·0	+12·5	3·6	–3
Azeotrope + PVP	6·3	/	6·3	/	6·3	/
Azeotrope + powder + PVP	9·0	+1·2	7·2	+1·5	4·9	+2·5



a) **A1N1SB2 —— 10 μm** b) **A1N2SB2 —— 10 μm**

c) **A2N1SB2 —— 10 μm** d) **A2N2SB2 —— 10 μm**

e) **A1N1SB2 —— 100 μm** f) **A1N2SB2 —— 100 μm**

Fig. 6. Microstructures of Al_2O_3–AlON–SiC composite sintered at 1710°C. (a) A1N1SB2, (b) A1N2SB2, (c) A2N1SB2, (d) A2N2SB2, and (e) A1N1SB2, (f) A1N2SB2 (low magnification).

affinity between these two components and, consequently, the stability and dispersion state of the slurry: the measurement of the variations of the pH allows prediction of what is the best powder/dispersant basis for a given medium and a given powder.

— electrophoretic measurement shows that the potentials developed at the powder surface are not sufficient to contribute to a good deflocculation. We must suppose that the steric stabilisation obtained by these polymeric dispersants is high enough.

— if the application of the best dispersion conditions to the binary mixture leads to a homogeneous material, in the presence of a ternary system it is not the same situation: an additional de-agglomeration stage allows a more homogeneous material.

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