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Progress in Powder Synthesis by w/o-Microemulsions

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Abstract

The formation of w/o-microemulsions for the synthesis of nanosized ceramic powders was investigated. Following the concept of HLB-(Hydrophilic-Lipophilic-Balance)numbers, w/o-microemulsions are formed by emulsifier mixtures with HLB-numbers between 8.9 and 10.0. The droplet size of the aqueous phase mainly depends on the emulsifier concentration and the amount of a cosurfactant. First precipitation experiments confirmed that nanocrystalline powders, such as Cr_2O_3 with a particle size around 20 nm, can be prepared by this technique.

1. INTRODUCTION

Materials with a nanosized microstructure have gained an increasing interest during the last few years, because they should show new and still unknown properties. This has been clearly demonstrated for nanocrystalline metals whose physical properties strongly differ from coarser materials [1 - 3]. In the field of ceramics, only little work has been carried out on the properties of nanocrystalline ceramic bodies, although some promising results like the preparation of ductile TiO_2 ceramics have been reported in the literature [4]. This can be attributed to the lack of sufficient powder quantities with a high quality which are essential for the development of suitable processing techniques and material testing.

For these purposes, large scale, inexpensive synthesis techniques of nanocrystalline powders must be developed. These techniques have to comply with the demands of advanced ceramic powders which are homogeneity, chemical purity, controlled particle size and morphology as well as state of agglomeration.

An interesting method for the preparation of ceramic powders has been reported in [5 - 6]. This technique uses the water-in-oil (w/o)-emulsion route. Thereby the droplet size of the aqueous phase, containing the desired ingredients in form of water soluble precursors, mainly defines the size of the ceramic particle derived by a precipitation process within the aqueous droplets. Different ceramic powders with particle size distributions ranging from 0.1 to 3.0 μm have been prepared by this technique [7 - 11].

On the other hand, only little attention has been directed

to the synthesis of nanosized ceramic powders, although different materials with particle sizes between 5 and 20 nanometers have been prepared from w/o-microemulsions covering metals, borides, sulfides, carbonates, and some oxides [12, 13].

The preparation of w/o-emulsions generally requires the use of surface active additives (emulsifiers) which reduce the interfacial tension of the two immiscible liquids by covering the aqueous phase with a thin film. The optimum stability and droplet size is determined by the interfacial tension between the emulsifier film and the aqueous phase as well as the oil phase. Therefore, the chemical properties of emulsifiers (hydrophilicity, lipophilicity) should match with those of the two phases. However, in order to comply with this requirement, emulsifiers must be selected very carefully. Suitable emulsifiers can be selected following the concept of HLB-(Hydrophilic-Lipophilic-Balance)-numbers because the hydrophilic-lipophilic-balance is an expression of the relative simultaneous attraction of an emulsifier for water and for oil [14]. Emulsifiers with low HLB-numbers (HLB < 9) are more lipophilic (o/w-emulsions) whereas emulsifiers with high HLB-numbers (HLB > 11) are more hydrophilic (w/o-emulsions). Emulsifiers with a HLB-number of 10 are hydrophilic and lipophilic as well. In order to form w/o-microemulsions, it was expected that the hydrophilic/lipophilic properties of the interfacial emulsifier layer must be balanced carefully. Two emulsifiers with largely different HLB-numbers but similar chemical structures were employed in this study in order to fit the hydrophilic/lipophilic properties at the water-to-oil interface. The goal was to develop a procedure for w/o-microemulsion preparations based on these emulsifiers and to ascertain the main parameters which determine the emulsion stability, achievable droplet size as well as the corresponding particle size.

2. EXPERIMENTAL

For the preparation of w/o-microemulsions, different amounts of Emulsogen OG (Hoechst), Tween 80 (ICI) and in some cases octanol were dissolved in petrolether (bp. 50 - 70 °C), followed by the addition of water or a 10 wt.-% aqueous solution of $Cr(NO_3)_3$. After combining the two phases, the mixture was stirred for 5 minutes and then ultrasonically agitated for additional 5 minutes. The volume fraction of each component was varied between 0 and 100 % for one overall volume of 200 ml. The stability of the emulsions was tested for a period of 24 h, and emulsions were called to be stable if no phase separation was visible.

Precipitation of chromiumhydroxide was carried out by bubbling gaseous ammonia through the emulsion. After the addition of 5 ml butanol, the residual water was evaporated by azeotropic distillation, followed by the evaporation of petrolether. The residual organic additives were burned out at 350 °C for 5 hours. Droplet and particle size distributions

after precipitation were measured by dynamic light scattering, and the calcined powder was studied by TEM.

3. RESULTS AND DISCUSSION

3.1 Formation of w/o-Microemulsions

The formation of w/o-emulsions was studied by using two nonionic emulsifiers with largely different HLB-numbers. Suitable emulsifiers seemed to be Tween 80 (HLB = 15.0) and Emulsogen OG (HLB = 3.0) because of their comparable chemical structures (Fig. 1) but different affinity to water and oil.

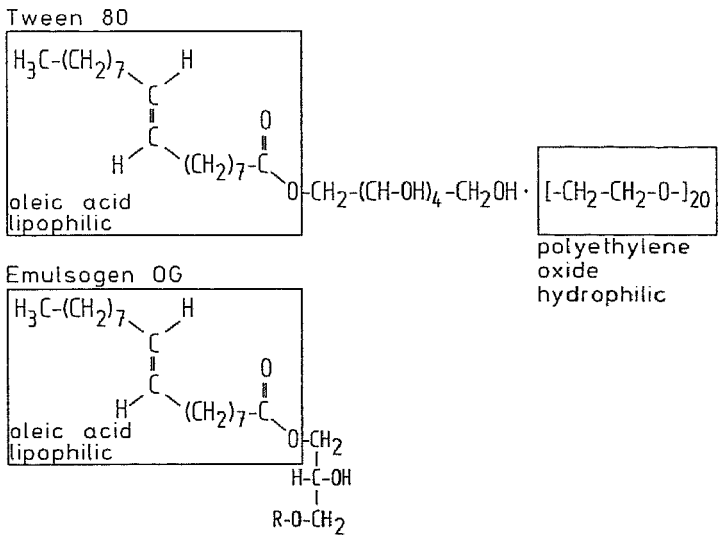

Figure 1: Chemical structures of Tween 80 and Emulsogen OG

As can be seen from Fig. 1, the chemical structure of the lipophilic parts of the emulsifiers are identical (oleic acid) and their hydrophilicity is adjusted by the chain length of the hydrophilic segment (polyethylene oxide block). Due to these structures, it was expected that the hydrophilic/lipophilic properties of the interfacial layer situated at the water-to-oil phase boundary can be varied by changing the volume ratio of the two emulsifiers.

Therefore, the formation of a stable emulsion was evaluated by varying the volume fractions of each emulsifier as well as the total amount (Fig. 2). The HLB-numbers of the emulsifier mixtures were calculated according to equation 1 [14] which allows the hydrophilicity/lipophilicity ratio from these data to be estimated.

$$HLB_{Mix} = \frac{V_{EOG}}{\delta_{EOG}} \cdot HLB_{EOG} + \frac{V_{Tween}}{\delta_{Tween}} \cdot HLB_{Tween} \quad (1)$$

with HLB_{Mix} : HLB-number of emulsifier mixture

HLB_{EOG}, HLB_{Tween} : HLB-number of emulsifiers

V_{EOG}, V_{Tween} : volume of emulsifiers

δ_{EOG}, δ_{Tween} : density of emulsifiers.

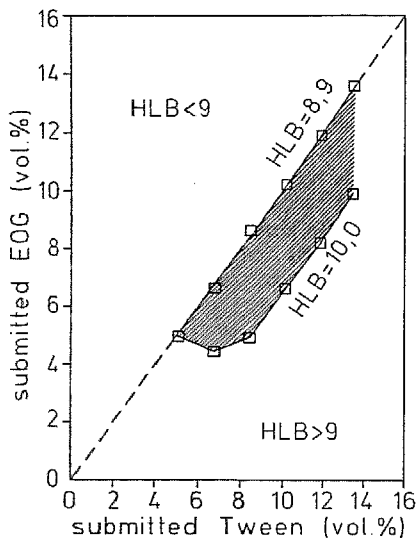

Figure 2: Region of stable w/o-emulsions for a constant w/o-ratio of 0.2.

It was found that stable w/o-emulsions are only formed if mixtures of emulsifiers are used. The region of stable emulsions is covered by HLB-numbers between 8.9 and 10.0, and a minimum amount of 11 vol.-% emulsifier is needed to form a stable emulsion. These results indicate that stable w/o-emulsions exist only in a limited range of HLB-numbers and can be explained by a model shown in Fig. 3.

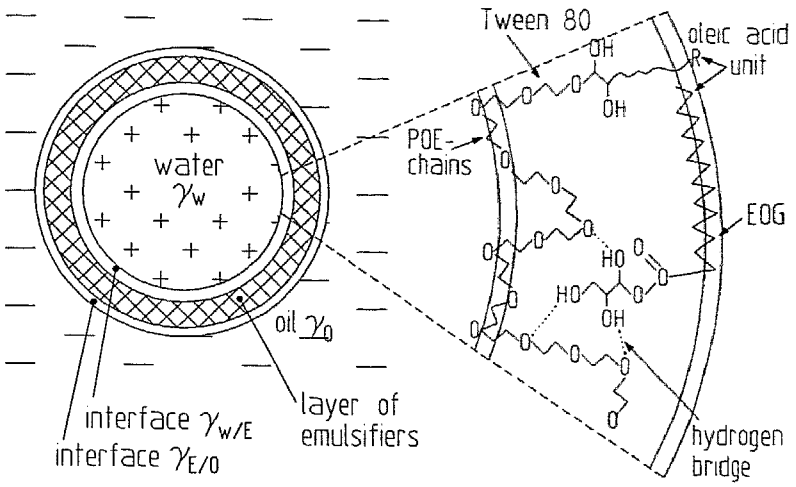

Figure 3: Model of emulsion stabilization by an emulsifier double layer

The emulsifier or a mixture of the two emulsifiers is adsorbed at the surface of the aqueous phase forming a thin film which lowers the interfacial tension between water and oil. This film can be treated as a separate phase having separate interfacial tensions at each of its sides ($\gamma_{W/E}$ and $\gamma_{E/O}$ in Fig. 3). Hence, the stability of the emulsion then depends on these interfacial tensions which can be correlated with the chemical structure of the emulsifier(s). From this point of view, it can be assumed that the maximum stability will be achieved if the hydrophilic and lipophilic segments of the emulsifier match with the chemical properties of the two phases. This requirement is not fulfilled by the single emulsifiers since no stable emulsions were obtained. On the other hand, stable w/o-emulsions could be prepared from mixtures of both emulsifiers indicating that the interfacial properties of the mixed emulsifier layer match quite well with those of the liquid phases at each of its sides. This can be explained in terms of the adsorption behavior of the emulsifiers at the water-to-oil interface as well as their interaction in the interfacial layer (Fig. 3). Therefore it is assumed that the hydrophilic polyethylene oxide block of Tween 80 is adsorbed preferentially at the surface of the aqueous droplets, and the lipophilic oleic/acid unit is turned towards the hydrocarbon. In addition to polyethylene oxide segments situated parallel to the water surface, tails and loops which are located within the interfacial layer can be formed, too.

On the other hand, adsorption of the lipophilic oleic acid segment of EOG should be preferred at the interface of the hydrocarbon. The hydrophilic part of this emulsifier might be located in the interfacial layer and there interacts with the polyethylene oxide loops and tools via hydrogen bridges formed between hydroxyl groups and polar oxygen atoms. This mechanism probably improves the interfacial properties of the emulsifier layer and leads to stable emulsions. However, this assumption must be confirmed by further experiments.

The next interesting question is related to the emulsion stability at fixed HLB-numbers.

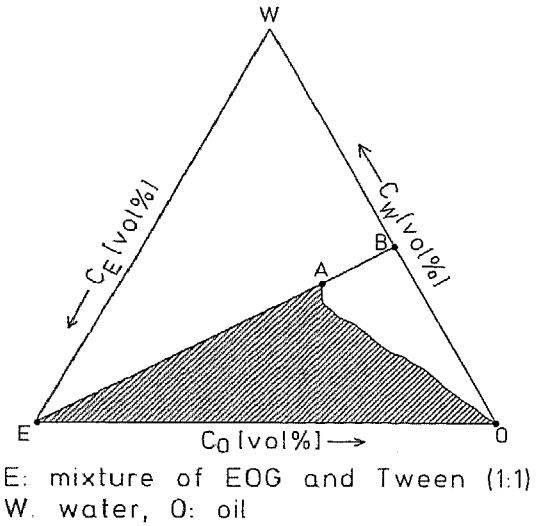

Figure 4: Phase diagram of stable w/o-emulsions for HLB = 8.9.

Therefore, the HLB-number of the emulsifier mixture was fixed at 8.9, and the W/E and W/O ratios were varied. It can be seen from Fig. 4 that the stability of the emulsion is limited by the water to emulsifier ratio (W/E) and the water to oil ratio (W/O). Stable emulsions are obtained for W/E ratio below 1.25 (line OA in Fig. 4). The limitation found for the W/O ratio of 0.8 (line EB in Fig. 4) corresponds with the inversion point of the emulsion which could be confirmed by conductivity measurements [14]. This means that above W/O ratios of 0.8, the emulsion is inverted from a w/o- to an o/w-emulsion, and the maximum water loading of the oil is fixed by this ratio. The effect of emulsifier concentration was investigated by dynamic light scattering [15] and the results are shown in Fig. 5 for W/O-ratios of 0.1 and 0.2, respectively.

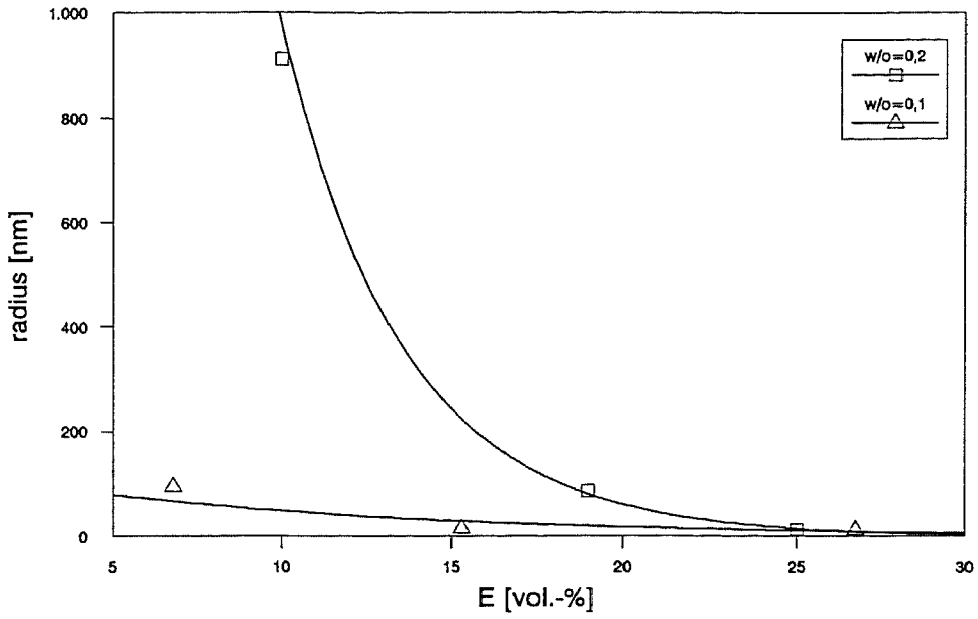

Figure 5: Droplet size as a function of emulsifier concentration for w/o-ratios of 0.1 and 0.2, respectively

The droplet size decreases with increasing emulsifier concentrations for both W/O-ratios, and this effect is more pronominal for the W/O-ratio of 0.2. In principle, this is not unexpected because with decreasing droplet size, the numbers of droplets as well as the surface area increases, and a higher amount of emulsifiers is needed for a complete covering of the droplet.

This decrease is also in agreement with smaller droplet sizes for the 0.1 W/O-ratio because a lower water concentration but constant emulsifier concentration correspond to an increase of the emulsifier.

An interesting effect was observed for the addition of small amounts of a cosurfactant like octanol. Cosurfactants are common agents for the preparation of microemulsions because they reduce the interfacial tensions $\gamma_{W/E}$ and $\gamma_{E/O}$ [4]. Fig 6 shows how the droplet size distribution changes on the addition of a small amount of octanol.

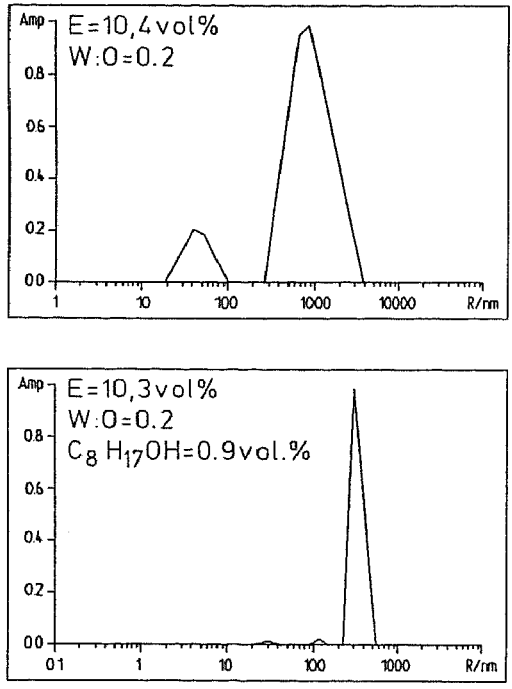

Figure 6: Effect of octanol on droplet size distribution

The broad and bimodal distribution (Fig. 6a) is turned to a monomodal distribution (Fig. 6b) and the droplet size decreases from an average value of 1 μm to an average value of about 300 nm. This can be attributed to a further improvement of the interaction between the emulsifiers due to the present octanol.

Based on these results, the influence of salt concentration on the emulsion quality was studied. Chromium nitrate was chosen for these experiments, and the salt concentration was fixed at 10 wt.-% and 20 wt.-%, respectively, with regard to the aqueous phase. In comparison to the above mentioned results, the emulsion stability is drastically decreased by the addition of the salt if no cosurfactant is used. On the other hand, stable emulsions were obtained with small amounts (1 - 5 vol.-%) of octanol. Again, monomodal droplet size distributions were found as shown in Fig. 7.

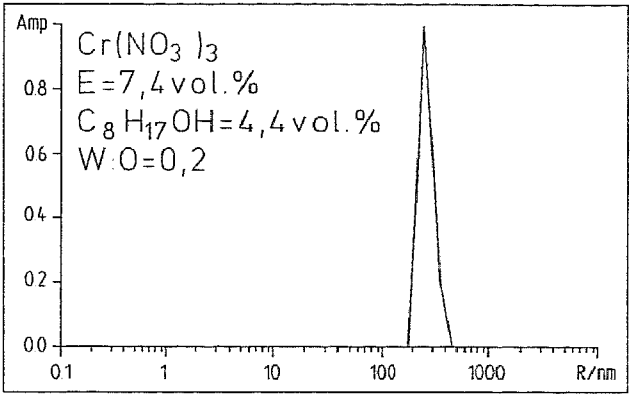

Figure 7: Droplet size distribution of a w/o-emulsion with 10 wt.-% $Cr(NO_3)_3$.

But in contrast to emulsions without salt loading, the cosurfactant cites a remarkable effect on the amount of emulsifier needed to achieve emulsions with comparable droplet sizes. The addition of only 1 vol.-% cosurfactant reduces the content of emulsifier from about 38 vol.-% to 19 vol.-%. In addition, the total amount of additives is lower, too.

From these results, it can be concluded that the stability and droplet size distribution in a w/o-emulsion is mainly influenced by the emulsifier concentration and its HLB-number. In addition, cosurfactants are suitable agents for improving the droplet size distribution and for reducing the amount of organic additives.

3.2 Precipitation of Nanosized Cr_2O_3

First precipitation experiments were carried out with a 10 wt.-% $Cr(NO_3)_3$ w/o-microemulsion by bubbling gaseous ammonia through it. The precipitates were densified in suspensions by azeotropic distillation of residual water. Precipitation and densification were followed by dynamic light scattering, and the results are shown in Fig. 8.

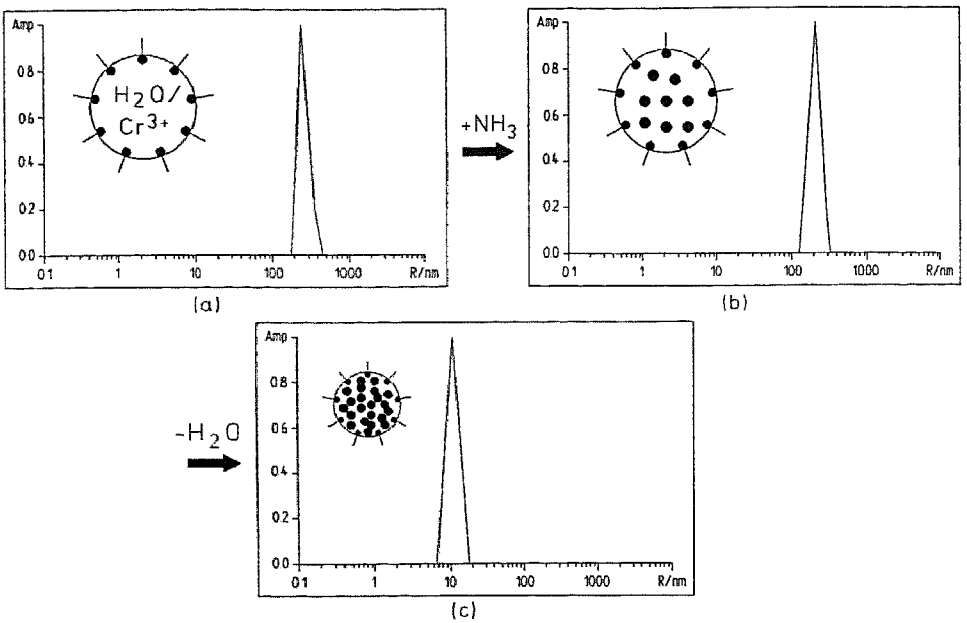

Figure 8: Change in droplet (particle) size after precipitation and densification of $Cr(OH)_3$.

a: w/o-microemulsion
b: after precipitation
c: after densification

The droplet size of the starting emulsion ranges from 200 to 450 nm and is only slightly shifted to smaller radii (180 - 400 nm) after precipitation. A tremendous decrease of particle size takes place during the densification step. Nanosized particles with a radius of about 10 nm are formed. This indicates that the precipitate inside the aqueous droplet is very loosely packed and can be densified by evaporation of water. Thus, it can be assumed that for the preparation of nanosized powders, the droplet size of the emulsion does not need to be equal to the desired particle size of the powder. TEM pictures (Fig. 9) of the calcined powder confirmed the particle radius of about 10 nm. The TEM-investigation also proves that the calcination process does not lead to a substantial agglomeration.

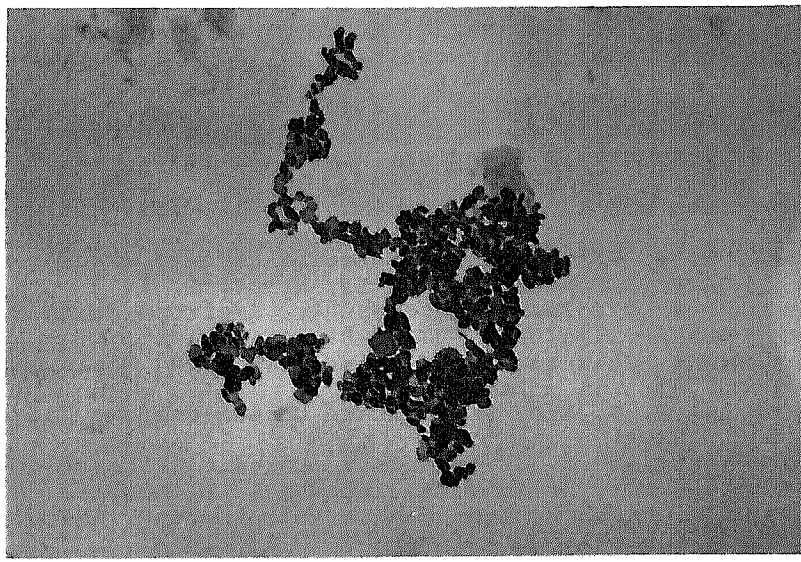

Fig. 9: TEM-picture of nanocrystalline Cr_2O_3 (⊢——⊣ = 200 nm).

4. CONCLUSION

The results of these investigations have shown that w/o-microemulsions can be developed easily when the HLB-concept is used for the selection of emulsifiers. The droplet size of the aqueous phase is mainly influenced by the emulsifier, but in the case of emulsifying aqueous salt solutions, the addition of long chained alcohols is essential and improves emulsion stability and reduces droplet size. It was shown that nanosized particles could be prepared not only in suspensions but could also be isolated and calcined without the formation of hard agglomerates. The whole process is considered to have an interesting potential for the chemical preparation of high grade nanosized powders.

5. REFERENCES

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