

Preparation, Characterization And Dielectric Properties Of The NiFe₂O₄/PMAs Hybrid Nanocomposite Film

Sema Vural¹, Mucahit Yilmaz²

^{1,2} Necmettin Erbakan University, Seydisehir AC Engineering Faculty, Metallurgical and Materials Engineering, Konya, 42360, Turkey

ABSTRACT

In this study, PMAs/NiFe₂O₄ nanocomposite was prepared using in-situ polymerization technique. The structure and morphological properties of nano composites were determined via FT-IR, SEM, EDX analysis methods. Thermal properties of prepared nanocomposites were investigated by TGA, DTA and DSC. Pure NiFe₂O₄ nanoparticles were synthesized using hydrothermal synthesis using the same conditions without monomers and characterized with the same methods for comparison. Prepared nanocomposites are structurally stable over one year. This effective synthesis strategy gives good opportunity to prepare highly stable magnetic nanocomposites.

Keywords: Nanocomposite, in-situ polymerization, magnetic composite.

1. INTRODUCTION

Spinel ferrites, NiFe₂O₄, combine a wide range of useful magnetic properties with relatively low electrical conductivity. Thus, unlike magnetic metals and alloys, they display low eddy current loss in alternating current applications and they are particularly useful in the radio frequency range. Therefore, the spinel ferrites have numerous applications in recording heads, core materials for various transformers, inductors and TV deflection units, and in recording tape [1]. It is suggested that nanoparticles possess a large surface to volume ratio, the surface disorder phase and non-magnetic layer would reduce the magnetization behavior of the material. It is suggested that magnetic properties of nano sized particles are largely depended on their crystallinity and homogenous dispersity of insulating media [2]. High technology hybrid materials are known for possessing a combination of good thermal, chemical, mechanical, and electronic properties, making them unique for certain technical applications [3]. Their usefulness, however, depends upon the characteristics of the nano powders. In general, to achieve desirable characteristics in the finished products, a nano powder should consist of particles with a narrow size distribution in the submicron or nanometer size range. In addition, to avoid pores larger than the primary particle size, the particles should be discrete, rather than attached together in agglomerated clusters [4-6].

However, nanometer particle-size powders are generally expensive and difficult to prepare in large quantities, thus limiting their applications to high technology ceramics. Accordingly, to extend the use and improve the function of such ceramics, a simple, low cost and up scalable process for making nanometer particle-size powders is desirable. In accordance with the process of this invention, a metal cation salt/polymer gel or colloid is formed by mixing an aqueous continuous phase comprising at least one metal cation salt with a hydrophilic organic polymeric disperse phase [7-10]. By the term "gel" as used throughout the specification and the claims, we mean a colloid in which a disperse phase is combined with a continuous phase to produce a viscous gel-like product. In the gel formed in accordance with the process of this invention, the disperse or colloidal phase is the hydrophilic organic polymer and the continuous phase is water. The metal cation salt is dissolved in the water [11]. When the hydrophilic organic polymer is added to the aqueous metal salt solution, a gel is formed by virtue of the gelling property of the polymer. In this process, the hydrophilic organic polymer absorbs the liquid on to its structure due to chemical affinity. The amount and nature of the water absorbed depends on the chemical composition of the polymer. The hydrophilic absorption of the water causes the polymer to swell [12].

We have determined that hydrophilic organic materials serve as good media for uniformly absorbing the metal ions of aqueous soluble salts. When a hydrophilic polymer is added to an aqueous metal salt solution, it swells as it absorbs the solution into its structure. The product is a gel with the metal salt solution "frozen" within the dispersed polymeric network. If the metal salt solution is dilute and the polymer added is not enough to gel the mixture, excess water may be dried off until the mixture is thick enough to form a gel. These metal oxide powders, as we have determined by use of an

electron microscope, are of nano size [13-15]. By nanometer particle-size powders, we mean powders having a predominate portion of particle sizes less than 100 nanometers in diameter [16-18].

2. EXPERIMENTAL

2.1. Instrumentation and Reagents

The chemicals used for the synthesis, $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 25% aqueous ammonia, meth acrylic acid, 35% hydrochloric acid, toluene (HPLC grade) and acetone, etc. were procured from Merck. All these chemicals were GR grade and were used without any further purification. The water used in all experiments was triply distilled and filtered from 0.22 μm size filter. The conductivity of water was below 0.2 $\mu\text{S cm}^{-1}$. The samples were characterized by X-ray diffraction (XRD) for the crystal structure, average particle size and the concentration of impurity compounds present. Rigaku Rad B-Dmax II powder X-ray diffractometer was used for X-ray diffraction patterns of these samples. The 2θ values were taken from 20° to 110° with a step size of 0.04° using Cu $K\alpha$ radiation (λ value of 2.2897 \AA). The dried samples were dusted on to plates with low background. A small quantity of $30(\pm 2)$ mg spread over 5 cm^2 area used to minimize error in peak location and also the broadening of peaks due to thickness of the sample is reduced. This data illustrate the crystal structure of the particles and also provides the inter-planar space, d . The broadening of the peak was related to the average diameter (L) of the particle according to Scherer's formula, i.e. $L = 0.9\lambda/\Delta \cos \theta$ where λ is X-ray wavelength, Δ is line broadening measured at half-height and θ is Bragg angle of the particles.

Infrared spectra were recorded as KBr pellets in the range $4000 - 400 \text{ cm}^{-1}$ on an ATI UNICAM systems 2000 Fourier transform spectrometer. Differential scanning calorimetry (DSC), differential thermal analysis (DTA) and thermogravimetry (TG) were performed with Shimadzu DSC-60, DTA-50 and TGA-50 thermal analyzers, respectively. Chemical composition analysis by EDAX was performed with an EDAX; Röntec xflash detector analyzer associated to a scanning electron microscope (SEM, Leo-Evo 40xVP). Incident electron beam energies from 3 to 30 keV had been used. In all cases, the beam was at normal incidence to the sample surface and the measurement time was 100 s. All the EDAX spectra were corrected by using the ZAF correction, which takes into account the influence of the matrix material on the obtained spectra. Cryogenic Q 3398 Vibrating Sample magnetometer (VSM) was used for magnetization measurements. These measurements were taken from 0 to ± 7 kOe fields. From these fields versus magnetization curve patterns, saturation magnetization values of the samples were measured.

2.2. Synthesis of hybrid materials

First 25 ml of 1M NaOH and 25 ml 1M methacrylic acid (MAs) mixed to produce meth acrylic acid sodium salt. Then 25 ml of this solution take into a Teflon lined stainless autoclave. $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in water at concentrations of 0.05 and 0.07 M, respectively. Fourteen milliliters of mixture salt solution was put into a Teflon lined stainless autoclave and mixed together. Autoclave was heated to 194°C and put this temperature for 10 hours. NiFe_2O_4 nanoparticles and polymethacrylic acid (PMAs) was formed via in-situ polymerization. Autoclave was cooled to room temperature. Then polymeric film was prepared from the polymeric mixture. (NiFe_2O_4 : PMAs = 1:9) The film characterized with thermal analysis methods which are TGA, DTA and DSC. FT-IR was used to characterize film structure and EDX used to determining dispersion of NiFe_2O_4 nanoparticles

3. RESULTS AND DISCUSSION

3.1. Nanoparticle characterization

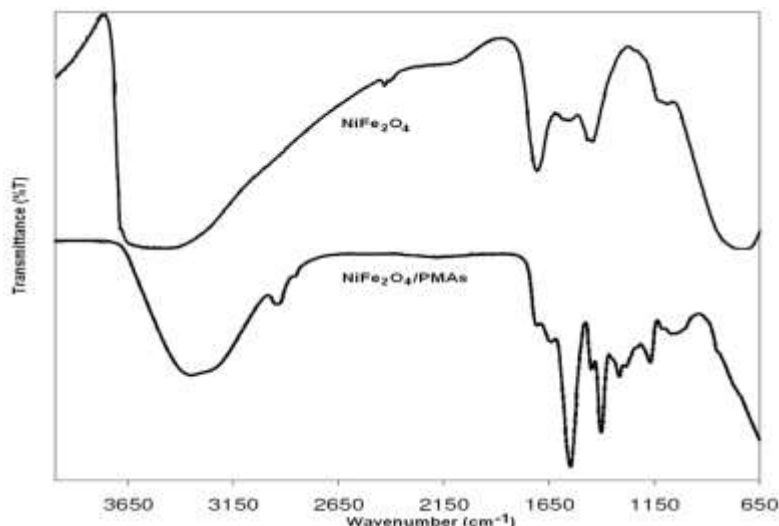


Figure 1. FT-IR spectra of NiFe_2O_4 particles, and $\text{NiFe}_2\text{O}_4/\text{PMAs}$ composite.

The FT-IR spectra (Fig. 1) showed that aliphatic C-H stretching frequencies were appeared between $2850-2890\text{ cm}^{-1}$, $1600-1650\text{ cm}^{-1}$ carbonyl ν (C=O) and $2900-3650\text{ cm}^{-1}$ hydrogen bond of the OH in carbonyl group ν (OH) stretching.

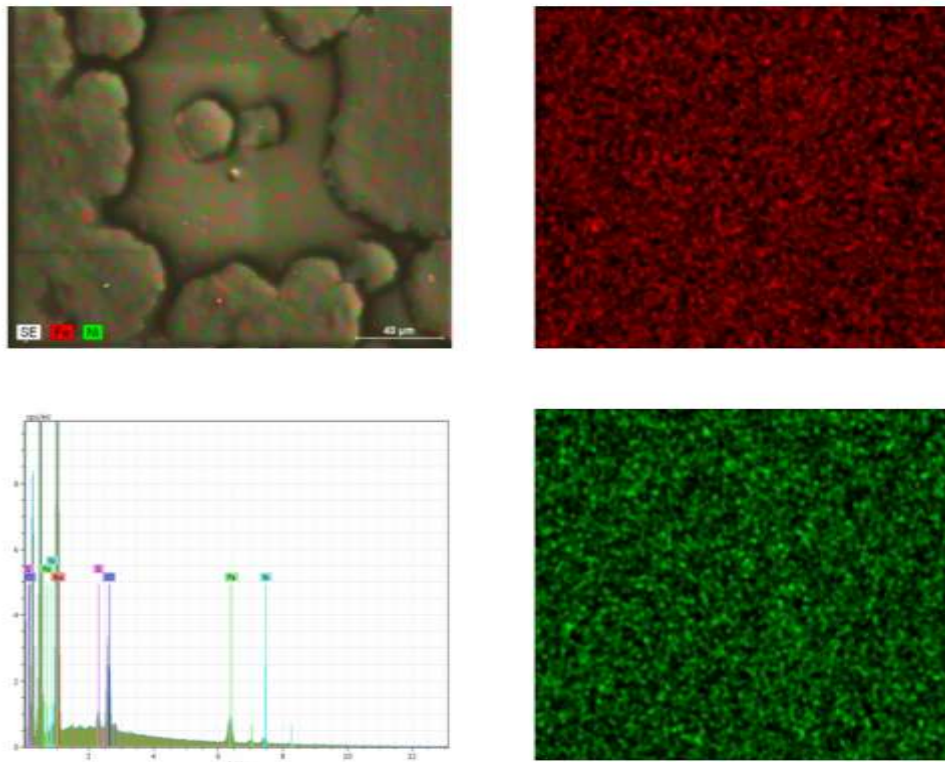


Figure 2. EDX (left) and mapping (right) results of NiFe_2O_4 -PMAs nanocomposite film. Dispersion of iron and nickel ions looking red and green, respectively.

Fig. 2 show scanning electron microscope (SEM) images of NiFe_2O_4 nanoparticles and NiFe_2O_4 nanoparticles embedded in the polymer matrix, respectively. It could be seen that NiFe_2O_4 particles were uniformly distributed throughout the PMAs matrix. There was no obvious aggregation of NiFe_2O_4 particles in the composites. The size of discrete phase was still remained in near sphere shape with diameter of 100 nm, the same to the original particles. With the increase of NiFe_2O_4 content, the packing of the particles grew denser. These results indicated the excellent compatibility between the polymethacrylic acid and the NiFe_2O_4 particles.

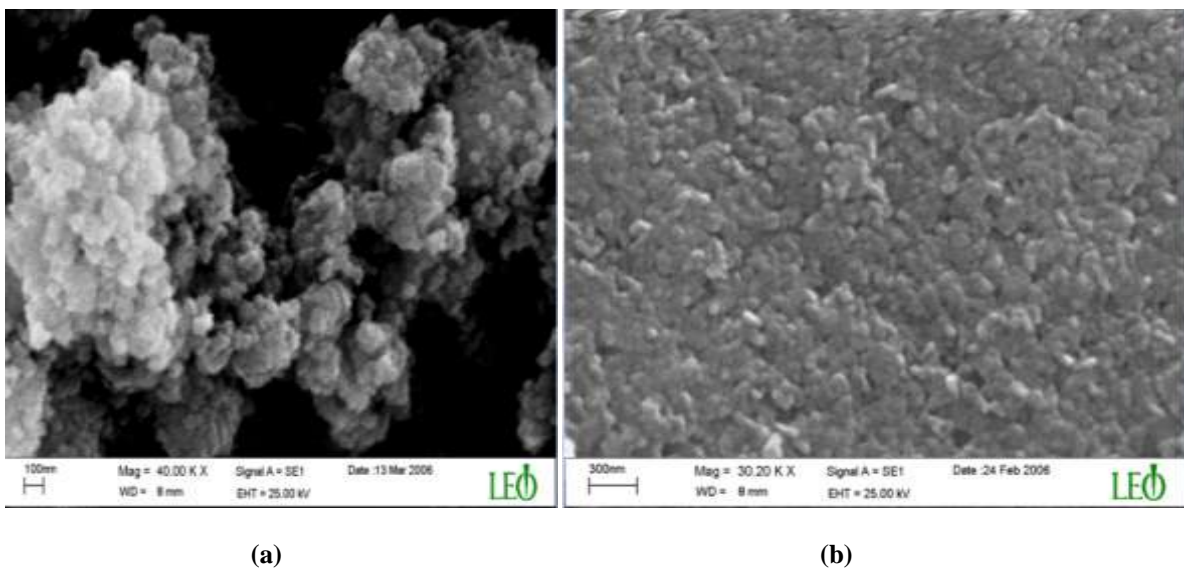


Figure 3. SEM image of the Ni_2FeO_4 nanoparticle (a) and NiFe_2O_4 /PMAs nanocomposite (b).

The thermal properties of the NiFe_2O_4 /PMAs nanocomposites and NiFe_2O_4 nanoparticles were evaluated by differential scanning calorimetry (DSC), differential thermal analysis (DTA) (Fig.4-5) and thermogravimetry (TG) (Fig.4-5).

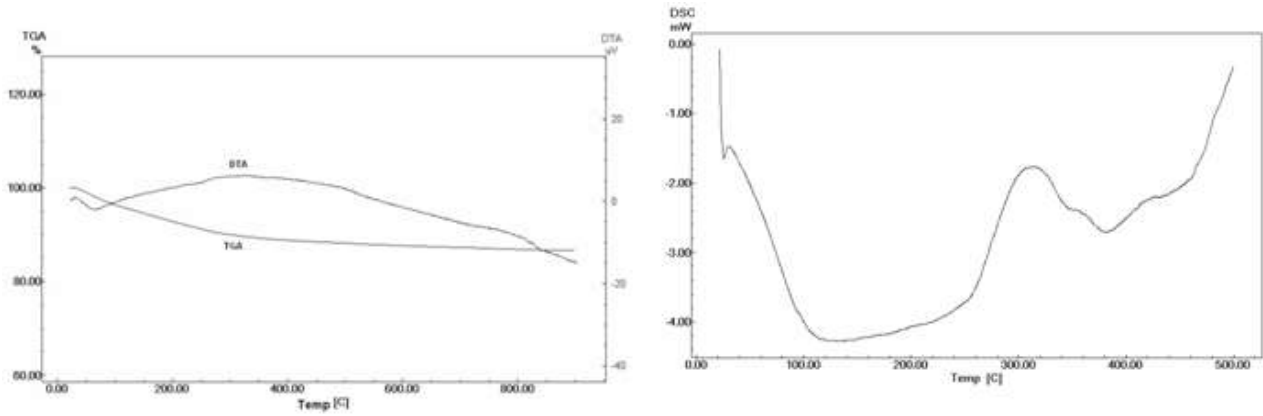


Figure 4. DTA, TGA thermograms and DSC measurement of NiFe₂O₄ nanoparticles

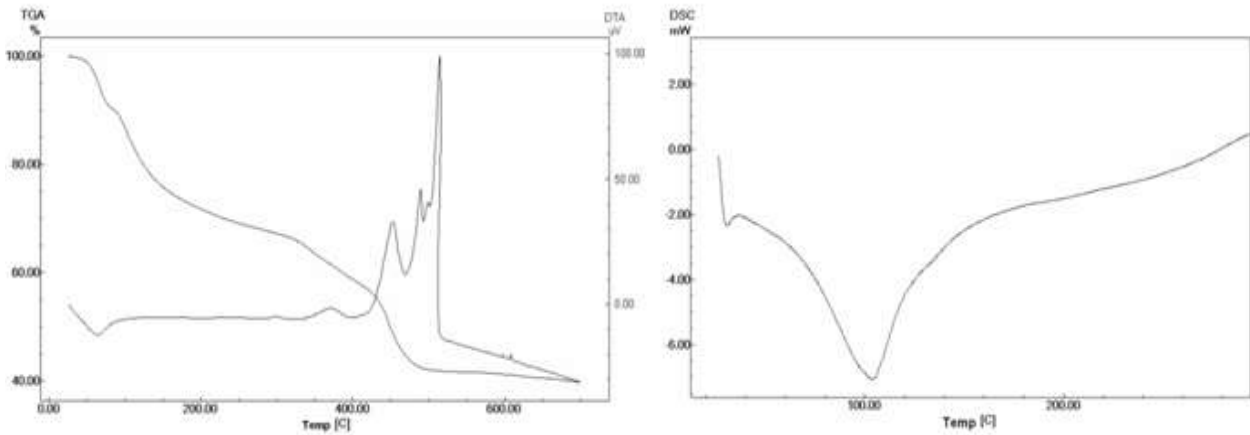


Figure 5. DTA, TGA thermograms and DSC measurement of NiFe₂O₄/PMAs nanocomposite

3.3. Dielectric properties of the nanoparticles

As shown in Fig. 7(a, b), the dielectric constant of the impregnated samples is highest than that of the pure PMAs. The NiFe₂O₄, porosity, average pore size, pore-size distribution, and residual alkali ions are factors that can affect the dielectric properties of NiFe₂O₄/PMAs. The hydrophobic properties of the PMAs, however, impart hydrolytic stability to the NiFe₂O₄-polymer combination, as shown for the dielectric characteristic in Fig. 7(b). Porous ceramics can be treated as mixtures of ideal dielectrics. In this case, assuming the dielectric constant of pores to be unity and that of bulk NiFe₂O₄, Banno [19] derived a theoretical equation that can be used to calculate the dielectric constant of porous gel-silica materials [20]. By applying the Banno equation to the impregnated and pure gel-silica samples, we calculated the dielectric constants of the samples with and without PMAs. A dielectric constant equal to 40.8, which is lower than the 45 experimentally measured.

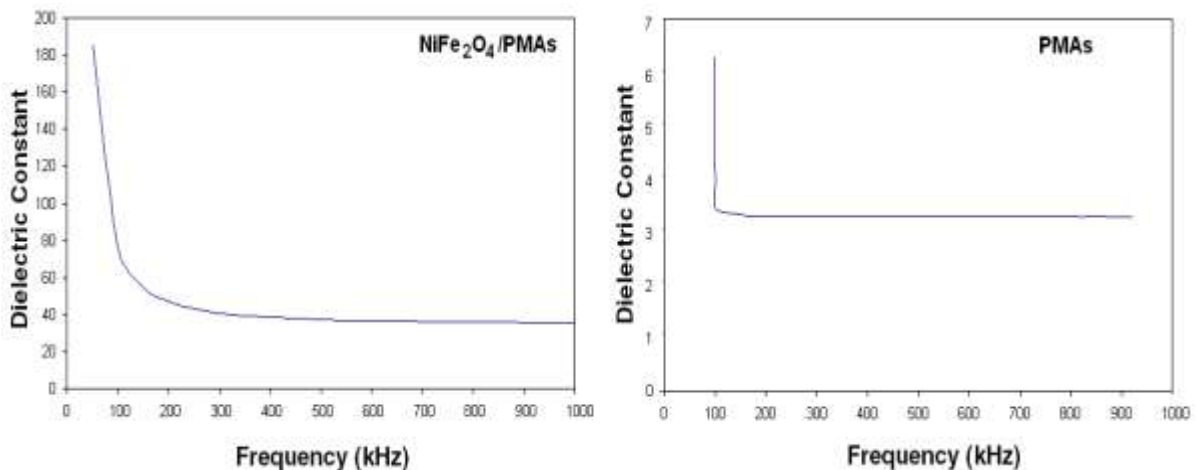


Figure 6. Variation of dielectric constant of pure PMAs and NiFe₂O₄/PMAs nanocomposite.

3.4. Stability of the NiFe₂O₄/PMAs nanocomposite solution

The sedimentation stability was examined by visual observation at a particle concentration of 10 vol%. The suspensions prepared using polymer solutions at 10 wt% were rapidly separated into clear supernatant solution and solid layers by sedimentation in the quiescent state. The times required for sedimentation were from several minutes to a few hours. The stock suspension without additives is electrostatically stabilized. The sedimentation of particles indicates that the addition of polymer causes the flocculation of suspensions. Since the PMAs chains can act as stickers of particles, the degree of flocculation is expected to increase with polymer concentration. However, at polymer concentrations of 2.0 wt% and above, the sedimentation was not observed, but the suspensions were very stable. The unique behavior of sedimentation stability implies that the particle-particle interactions and in turn the flocculating power decrease as the polymer concentration is increased above some level. (Figure 7)

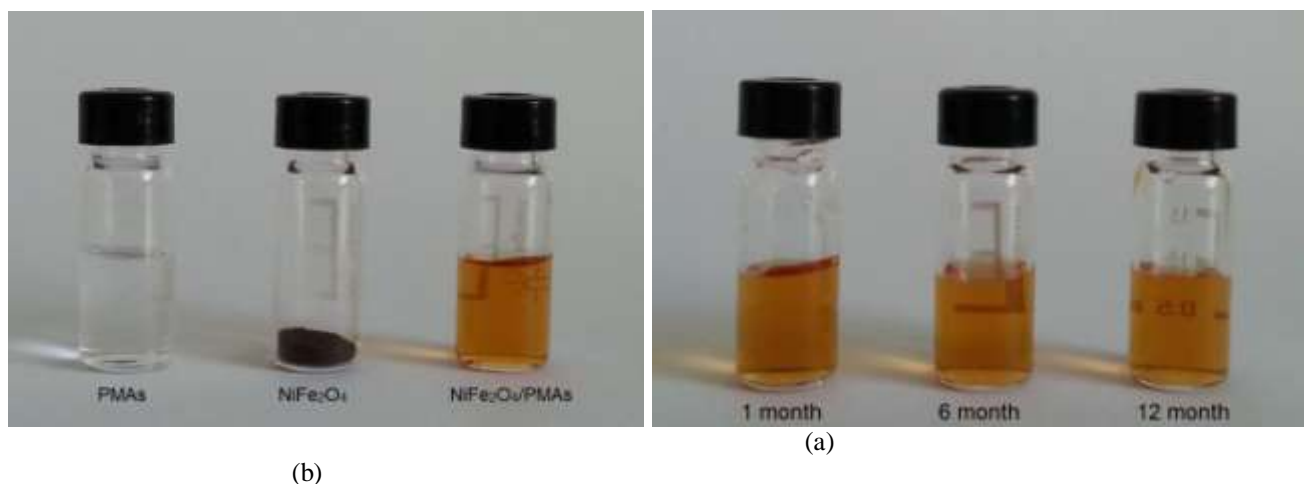


Figure 7. (a) Vials containing PMAs, NiFe₂O₄ and NiFe₂O₄/PMAs, (b) Vials containing NiFe₂O₄/PMAs. There are not clear differences in various time (1 m, 6 m and 1 year).

CONCLUSION

We have determined that hydrophilic organic materials serve as good media for uniformly absorbing the metal ions of aqueous soluble salts. When a hydrophilic polymer is added to an aqueous metal salt solution, it swells as it absorbs the solution into its structure. The product is a gel with the metal salt solution "frozen" within the dispersed polymeric network. If the metal salt solution is dilute and the polymer added is not enough to gel the mixture, excess water may be dried off until the mixture is thick enough to form a gel. These metal oxide powders, as we have determined by use of an electron microscope, are of nano size. By nanometer particle-size powders, we mean powders having a predominate portion of particle sizes less than 100 nanometers in diameter.

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