

Polymers for Stabilization of Colloidal Cobalt Particles

PATRICK H. HESS* and P. HAROLD PARKER, JR.,
Chevron Research Company, Richmond, California 94802

Synopsis

A process for preparing metallic cobalt particles of uniform size in the 10–1000 Å. range is described. Dicobalt octacarbonyl is thermally decomposed in solutions of dispersant polymers to form stable colloids of discrete particles which are separated by polymer coatings. Variation of polymer composition, molecular weight, and solvent used results in a variation of particle size and colloid stability. Preparation of single-domain ferromagnetic cobalt particles with good magnetic properties depends on a very delicate balance between dispersant polymer, solvent, and the growing metal particle. A number of addition and condensation polymers can act as dispersants. The most successful are linear addition polymers of high molecular weight having relatively nonpolar backbones. Ideally, groups with a polarity greater than the backbone are attached at intervals of at least 100 but not more than 200 backbone atoms. The need for more polar groups and their spacing becomes less critical with increasing polymer molecular weight. The polymers appear to stabilize the metal particles by adsorption to form a thick film which separates the particles sufficiently to keep van der Waals energy of attraction below thermal energy levels. The solvent must solubilize the polymer coating sufficiently to allow the particle to grow. It should be less polar than the most polar group in the polymer and be chemically inert.

INTRODUCTION

Unique systems composed of metallic cobalt particles of surprisingly uniform size have been prepared by the thermal decomposition of dicobalt octacarbonyl in solutions containing polymeric materials.^{1,2} The product is a black, stable colloid of metallic cobalt particles, predominantly of face-centered cubic crystal structure.³ The particles are discrete, being separated by coatings of polymer.

By varying polymer composition, average molecular weight, and solvent used, the average particle size may be varied over the range of about 10–1000 Å. Usually about 85 wt.-% of the particles will be within a factor of two of the average particle size.^{1,2}

Cobalt particles with sizes less than about 600 Å. (this varies somewhat with the shape) are single-domain in character and possess a net magnetic moment. In single-domain cobalt particles with sizes greater than about 100 Å., this moment becomes greater than thermal energy levels, and the

* Present address: Chevron Research Company, La Habra, California.

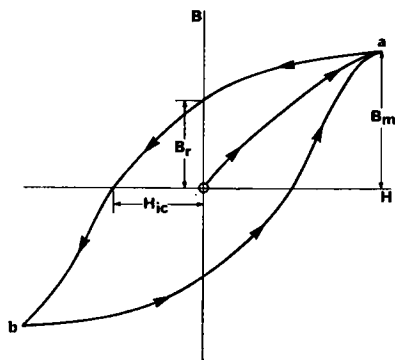


Fig. 1. Hysteresis loop of a ferromagnetic material.

particles, through dipole-dipole interaction, tend to form into linear chains.³ These products are excellent permanent magnets and are ideally suited for use as magnetic inks, as coatings in magnetic recording devices (tapes, disks, drums), as magnetic pigments or embedments, etc.^{1,2}

Magnetic properties used to describe single-domain cobalt particles in this publication will be defined with the aid of the hysteresis loop (Fig. 1). When an initially unmagnetized ferromagnetic sample is placed in a field of increasing magnetizing force H , the magnetic induction or flux density B of the sample also increases, not linearly, to an induction value B_m (point a). If the applied field is then reduced toward zero, the induction curve does not retrace the original curve but lags behind it (ab). When the applied field returns to zero, the sample retains a residual induction or remanence B_r , which is proportional to the amount of permanent magnetization induced in the sample by the applied field. For permanent magnets a high remanence ratio B_r/B_m is most desirable.

As the applied field is increased in the reversed direction, the induction of the sample continues to decrease. The reversed magnetizing force required to reduce sample induction to zero is called the intrinsic coercive force H_{ic} . The intensity of this force is a measure of the magnetic permanence or the resistance to demagnetization of the sample. For permanent magnets a high coercive force is desirable.

Thorough discussions of ferromagnetic materials are presented in numerous books and articles. Single-domain particles are discussed by Kittel and Galt.⁴ Elongated magnetic particles are discussed by Luborsky⁵ and by Jacobs and Bean.⁶ Magnetic properties of the single-domain cobalt particles described in this article are discussed more thoroughly by Thomas.³

Electron photomicrographs of colloidal cobalt particles prepared by the method described are shown (Fig. 2). In Figure 2A the majority of the particles are less than 100 Å.; this product has a coercive force of 60 oersted and a remanence ratio of 0.07. In the product shown in Figure 2B, the average particle size is larger and chains have formed which have a pronounced effect on magnetic permanence ($H_{ic} = 135$ oersted; $B_r/B_m =$

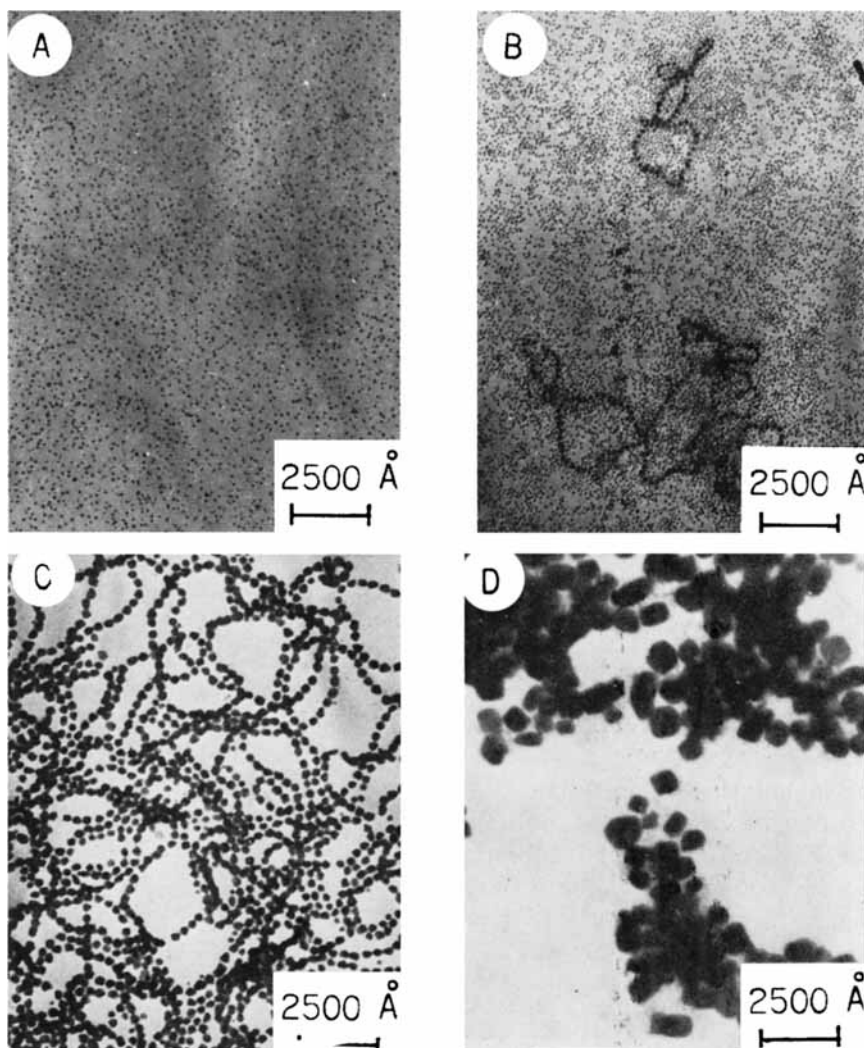


Fig. 2. Electron photomicrograph of colloidal metallic cobalt particles. 40,000 \times .

0.37). Cobalt particles shown in Figure 2C are in the 200–400 Å range and have chained extensively. This product has excellent magnetic properties ($H_{ic} = 408$ oersted; $B_r/B_m = 0.57$). Many of the particles shown in Figure 4D are multidomain. These large particles result in a decrease in magnetic remanence ($H_{ic} = 281$ oersted; $B_r/B_m = 0.12$).

Little is known of the mechanism of colloid stabilization in media of low dielectric constant.³ Copolymers of reasonably high molecular weight furnish a high degree of stability to such colloids and are outstanding dispersants for use in automotive lubricating oils.⁷ The effectiveness of such copolymers appears to be related to the thick, solvent-swollen copolymer films adsorbed on the particle surface.⁸ Colloid stabilization occurs when

the film is of thickness sufficient to increase the particle separation and thus decrease the van der Waals energy of attraction to below thermal energy levels.

In this investigation a variety of polymeric materials were studied as stabilizers for colloidal cobalt particles. Experimental techniques are outlined, and results are discussed. Possible reasons for the relative effectiveness of various polymers as colloid stabilizers, based on polymer composition and polymer-solvent-metal interactions, are presented.

EXPERIMENTAL

Polymer Preparation

Methyl Methacrylate-Ethyl Acrylate-Vinylpyrrolidone Terpolymers. Inhibitors were extracted from the acrylic monomers with 2% aqueous potassium hydroxide. The monomers were washed with distilled water, then dried over anhydrous calcium sulfate. *N*-vinyl-2-pyrrolidone was used as supplied.

All of the vinylpyrrolidone and proportional amounts of methyl methacrylate, ethyl acrylate, and methyl ethyl ketone solvent were charged to a three-necked, round-bottomed flask equipped with a mechanical stirrer, a dropping funnel, a buret, a reflux condenser, and a heating mantle. After heating the solution to reflux, with stirring, a portion of 2,2'-azobis-(2-methylpropionitrile) in methyl ethyl ketone was added over a 6-hr. period, while methyl methacrylate and ethyl acrylate in methyl ethyl ketone solution were added simultaneously over the first 5 hr. The product solution was then poured into *n*-pentane. Precipitated polymer was redissolved into toluene, then reprecipitated in *n*-pentane. After redissolving and reprecipitating several times, the polymer was dissolved in toluene and the solution heated to remove excess pentane. The solution was filtered and per cent solid was determined. Polymer was characterized by nuclear magnetic resonance spectra and nitrogen analysis; polymer molecular weight was determined by viscosity measurements.

High-Purity Polystyrene. Inhibitor was removed from styrene monomer by extraction with 2% aqueous potassium hydroxide. The monomer was water washed, dried over anhydrous calcium sulfate, then vacuum-distilled from copper turnings. The center cut of distillate was retained for use in polymerizations.

Purified styrene monomer was placed in a glass ampule and was deoxygenated by repeated cycles of freezing, high vacuum, and thawing in a nitrogen atmosphere. The ampule was sealed and the styrene was held at 100°C. for 24 hr. The thick, syrupy product was dissolved in toluene, precipitated in methanol, redissolved, and reprecipitated three times, then finally dissolved in toluene. Total solid in the solution was determined. Polystyrene molecular weight was determined by viscosity measurements.

Styrene-Acrylonitrile Polymers. Styrene and acrylonitrile monomers were purified by distilling from copper turnings. The monomers were

copolymerized in toluene solution by a technique similar to that used in preparing the acrylic terpolymers.

Polyacrylonitrile. Polyacrylonitrile was prepared by using a slurry technique as outlined in Sorenson and Campbell.¹⁰

Chloropoly(ethylene Sulfonamide). To 20 g. of a chlorosulfonated polyethylene (du Pont Hypalon 30) in 200 ml. xylene was added 50 ml. of piperidine. The solution was refluxed for 3 hr. Polymer was precipitated by pouring into 1500 ml. of methanol. Solvent was removed by decantation. The polymer was washed three times with 500-ml. portions of methanol and was dried under vacuum for 64 hr. at 50°C. The sulfonyl chloride groups were essentially quantitatively converted to sulfonamide groups.

Polyester and Polyether Urethanes. Equimolar amounts of a dry polyether or polyester of molecular weight 4000 and *p,p'*-diphenylmethane diisocyanate were mixed with 4 mole-% triethylenediamine catalyst and 15 times their volume of dry toluene and refluxed for 24 hr. Solvent was evaporated, and the oily polymer was dissolved in toluene.

Other Polymers. Other polymers studied were commercial products as shown in Table I.

Cobalt Particle Preparation

Dicobalt octacarbonyl crystals (23.5 g.) were dissolved in the solvent (Table I) to make 188 ml. of solution. This solution was placed in a 500-ml., three-necked, round-bottomed flask equipped with a mechanical blade stirrer and a reflux condenser. To this solution was added, with stirring, sufficient polymer dissolved in the same solvent to yield the desired metal-to-polymer ratio in the final product. Additives were included in the reaction solution where indicated. The flask was closed and stirring continued at room temperature for about 5 min.

The contents of the flask were rapidly heated to a fast reflux. During heatup and decomposition, the reaction mixture was agitated as thoroughly as possible. One molar equivalent of carbon monoxide evolved very rapidly, as measured by a wet test meter. The remaining carbon monoxide evolved at a slower, fairly constant rate. When gas evolution ceased, the product mixture was cooled with continued stirring. The cooled mixture was held in glass bottles for testing.

Magnetic Properties

A portion of cobalt particle sample was stirred in a high shear blender (Omni-Mixer, Ivan Sorvall, Inc.) for 1 min. This mixture was coated on 1-mil Mylar film by using a Baker paint applicator with gate set to give a dry coating of 0.1–0.2 mil thickness. The coating was dried by evaporation, the final solvent being evaporated with the aid of an infrared heat lamp.

Intrinsic coercive force H_{ic} and remanence ratio B_r/B_m of the coated particles were measured with the aid of a B-H meter (Scientific Atlanta, Inc., Model 651B) with a 2000-gauss field strength.

TABLE I
Polymers for Stabilization of Colloidal Metallic Cobalt Particles

No.	Polymer type	\bar{M}	Solvent	Metal in solids, %	Coercive force, oersted	Remanence ratio	Size range, A.
Control							
1	No polymer	—	Toluene	100	100 (est.)	—	>1000
Addition polymers							
Methyl methacrylate-ethyl acrylate-vinylpyrrolidone							
2A	33/66/1	300,000	Toluene	75	316	0.58	150-400
2B	33/66/1	300,000	Toluene ^a	75	498	0.65	150-400
2C	33/66/1	300,000	Chlorobenzene	75	307	0.54	150-400
2D	0/90/10	100,000	Chlorobenzene	75	165	0.51	60-250
3A	Polychloroprene	380,000	Toluene	75	723	0.51	300-600
3B	Polychloroprene	380,000	Toluene	83	573	0.54	300-600
3C	Polychloroprene	380,000	Toluene	93	261	—	300-600
Chlorovinyl							
4A	Vinyl chloride-acetate-alcohol, 91/6/3	—	Chlorobenzene	75	219	0.47	70-470
4B	Vinylidene chloride-acrylonitrile, 88/12	—	MIBK	75	257	0.18	—
Chlorosulfonated polyethylene							
5A	Sulfonamide	21,000	Toluene	75	557	0.39	60-300
5B	Sulfonyl chloride	—	Toluene	75	396	0.45	—
Styrene-acrylonitrile							
6A	100/0	476,000	Toluene	75	366	0.25	100-300
6B	92/8	100,000	Toluene	75	50	—	60-130
6C	88/12	100,000	Toluene	75	10	—	60-130
6D	61/39	100,000	DMF	75	—	— ^b	— ^b
6E	0/100	150,000	DMF	75	—	— ^b	— ^b
7	Atactic polypropylene	5,000	Toluene	75	—	—	>1000

Condensation polymers						
Polyethers						
8A	Ethyleneoxydiol	600	Toluene	75	—	—
8B	Ethyleneoxydiol	6,800	Toluene	75	400	300-700
8C	Ethyleneoxydiol	6,800	Toluene ^a	75	331	—
8D	Propyleneoxydiol	400	Toluene	75	258	60-200
8E	Propyleneoxydiol	3,000	Toluene	75	254	70-300
8F	Propyleneoxytriol	440	Toluene	75	385	70-400
8G	Propyleneoxytriol	6,000	Toluene	75	246	70-450
8H	Propyleneoxypentol	590	Toluene	75	—	—
Urethanes						
9A	Polyester urethane	—	Toluene	75	254	—
9B	Polyether urethane	~20,000	Toluene	75	354	250->1000
9C	Polyester isocyanate	1,000	Toluene	75	—	—
9D	Polyester isocyanate	1,000	Toluene ^a	75	142	50-300
9E	Urethane rubber	—	Toluene	75	—	—
10	Urea-formaldehyde	—	Toluene	75	404	100-200
Polyesters						
11A	Polyhydroxy polyester	2,500	Toluene	75	311	100-200
11B	Terephthalic/isophthalic/ ethylene glycol, 9/1/10	—	Toluene	75	258	—
11C	Alkyd	4,000	Toluene	75	173	70-180
12	Bisphenol-A polycarbonate	50,000	Chlorobenzene	75	385	80-450
13	Starch	—	Toluene	75	235	120->1000
14	Silicone	—	Toluene	75	192	—
15	Bisphenol-A epoxy	1,000	Toluene	75	—	—
16	Aminoamide	—	Toluene	75	—	—

^a Additive: methyl isobutyl ketone (MIBK), 2.5 vol.-%.

^b Metal reacted with the solvent.

Particle Size Determination

A 1-ml. portion of cobalt particle sample was added to 9 ml. of the solvent in which it was prepared. After shaking, a drop of the mixture was smeared on an electron microscope sample grid (Formvar Substrate, Ladd Research Industries). After drying, electron photomicrographs of the sample were prepared with the use of a J.E.M. Model 6A electron microscope. Wherever possible, a 40,000 magnification was used. When agglomerates were found, edges where individual particles were visible were photographed. Partial sizes were determined by measurements from the photomicrographs.

RESULTS AND DISCUSSION

Typical cobalt particle preparations with a number of addition and condensation polymer dispersants are outlined in Table I. Listed are polymer compositions and molecular weights where available, the reaction solvent, additive and concentration when used, and the anticipated metal concentration in the product. Also listed are the criteria for judging the effectiveness of the polymer as a media for producing single domain cobalt particles with unique magnetic properties. These criteria are particle size range as determined by electron photomicroscopy, the intrinsic coercive force H_{ic} , and remanence ratio B_r/B_m of the coated product.

If no dispersant polymer is present during the carbonyl decomposition reaction, large multidomain cobalt particles are formed. These materials are of no use as permanent magnets.

Several polymers do not yield magnetically interesting products; however, a majority of the polymers studied do yield cobalt particles in the single-domain size range, and a number of these give cobalt particles which associate into chained particle structures with high coercive forces and remanence ratios.

From consideration of the data, it appears that formation of single-domain cobalt particles and their arrangement into particle chains are dependent on a very delicate polymer-solvent-metal balance. Polymers and solvents will be considered separately below.

Polymers

Polymers which act as dispersants for single-domain cobalt particles have definite characteristics. Consideration of the polymers studied leads to some conclusions about these desired characteristics.

The most successful dispersant polymers, as judged by cobalt particle size distribution and particle magnetic properties, are the addition polymers with average molecular weights of 100,000 or more. The best of these polymers are composed of a relatively nonpolar backbone with nonreactive polar groups attached to alternate carbons on this backbone. Very polar groups are attached at wider intervals. The spacing of these very polar

groups does not seem to be critical, but at least one very polar group every 200 backbone carbon atoms is minimum. The polymer molecular weight should be sufficiently high to allow some of the polar groups to adsorb onto the metal surface, leaving the bulk of the polymer to form a thick coating and thus protect the metal particles from agglomeration.

Acrylic terpolymer of methyl methacrylate, ethyl acrylate, and vinylpyrrolidone is the best example of this type of dispersant polymer. This material appears to coat the metal with a thick film of polymer resulting in a very stable colloid. The terpolymer has a polyethylene backbone with pendant polar ester groups every two backbone carbon atoms and a very polar amide group every 200 backbone carbon atoms. The polar amide groups evidently adsorb onto the metal surface. The bulk of the polymer chain extends into the liquid phase forming a thick, solvent-swollen coating.

Size of the cobalt particles can, to some extent, be controlled by the concentration of polar groups in the polymer. This is illustrated by the 90/10 ethyl acrylate-vinylpyrrolidone copolymer. The smaller particle size probably results from the increased concentration of amide groups on the metal surface sterically hindering carbonyl decomposition at the metal surface, thereby retarding particle growth.

Polychloroprene is another example of a high molecular weight addition polymer yielding particles with particularly excellent size, coercive force, and remanence ratio. Polychloroprene does not result in colloid stability comparable to that of the acrylic terpolymer, but the spacing of polar groups and molecular weight in this rubber seems to be particularly right for growing cobalt particles to the proper size and allowing these particles to chain. It is not known whether the adsorbing species in this polymer is the moderately polar chlorine group, spaced every four backbone carbon atoms, or the 1% oxygen content in this commercial product which may be present as a more polar group spaced along the backbone.

Increasing the metal content in the polychloroprene product from 75% to 93% results in a corresponding decrease in coercive force. Decreasing the thickness of the polymer sheath around the cobalt particle probably results in a less stable colloidal dispersion, and consequently the product undergoes a lesser degree of linear particle chaining.

Vinyl chloride-vinyl acetate-vinyl alcohol terpolymer yields cobalt particles with some superparamagnetic particle content (particle size less than about 100 Å.). Chaining does not occur, and the product coercive force is low. This may be the result of polar group concentration being too high in this polymer.

Vinylidene chloride-acrylonitrile copolymer in methyl isobutyl ketone results in a product with very low remanence ratio. Again, this may be due to too high a concentration of polar groups in the polymer, or the very polar solvent may have competed too well with the nitrile groups for adsorption onto the metal surface. Also, the high-energy cobalt particles may have reacted with the polymer, possibly through removal of a *gem*-chlorine group.

Polystyrene and styrene-acrylonitrile copolymers give additional information as to dispersant mechanism. Polystyrene was prepared by thermal polymerization, care being taken to prepare as pure a homopolymer as possible. This relatively nonpolar polymer (although certainly not as nonpolar as polypropylene) yields cobalt particles in the proper size range with fairly good magnetic properties. In this case the high molecular weight of the polymer, in combination with its phenyl-substituted backbone, apparently leads to thick, solvent-swollen stabilizing coatings around the cobalt particles.

The high molecular weight of the polystyrene may to some extent account for the stabilizing action. At very high molecular weights the statistical probability of forming a thin, flat film may be low, and the occurrence of chains extended as loops from the metal surface may be higher, which gives a thick coating and better dispersion.

Inclusion of acrylonitrile into the styrene polymer yields very small particles which are superparamagnetic. This may be due to the high concentration of very polar groups in the copolymers.

Spacing of polar groups is more critical for dispersant polymers in the 10,000–50,000 average molecular weight range than for the high molecular weight polymers. For use in toluene solution, the most polar groups in the polymer should be spaced every 100–200 backbone carbon atoms. Polar groups may be in the backbone or pendent from the backbone. These dispersant polymers are more effective when the most polar constituents are other than endgroups. The endgroup concentration is probably too low for the endgroup to act as a more polar group in polymers of high molecular weight.

Polyether urethane fits this description of a satisfactory dispersant, having a poly(ethylene oxide) backbone connected every 200 backbone carbon atoms with a highly polar urethane group. That the polyester urethane of comparable molecular weight led to a poorer product may be due to the greater difference in polarity between ether and urethane groups than between ester and urethane groups.

Chlorinated poly(ethylene sulfonamide) also fits the description of a medium molecular weight dispersant polymer, having sulfonamide groups pendent every 100 backbone atoms. That the sulfonamide product was superior to the sulfonyl chloride dispersion illustrates the improvement resulting from the addition of a small amount of a more polar group to the polymer backbone.

Bisphenol-A polycarbonate led to a surprisingly good magnetic cobalt product. This illustrates that a fairly good dispersion can be prepared with a polymer having a polyester-type backbone and no other polar groups if the polymer molecular weight is high enough. It is possible that the relatively rigid backbone of this polymer may contribute to a polymer chain more extended from the surface and thus to a thicker coating.

In the average molecular weight range of 100–6000, the polymer type and the spacing and polarity of polar groups are quite critical. Higher molecular weight diols of poly(ethylene oxide) and poly(propylene oxide)

yield a better product than the lower molecular weight polymers. Polypropyleneoxytriol is a much better dispersant at low molecular weights than the diols. Polypropyleneoxypentol does not act as a dispersant.

Low molecular weight polyesters do not disperse cobalt particles as well as some of the low molecular weight polyethers. This is probably because the hydroxyl or carboxylic acid endgroups act as spaced groups of higher polarity. The endgroups have a greater difference in polarity when compared with the nonpolar polyether backbone chain than they do when compared with the more polar polyester backbone.

The urea-formaldehyde polymer may be an example of a branched structure which cannot easily form a thin coating because its geometry is more likely to give polymer chains extending from the surface to form a thick coating. The alkyd may also belong to this class.

Silicone grease, bisphenol-A epoxy, and polyaminoamide failed to disperse cobalt. The latter may have reacted with the metal. Atactic polypropylene was little better as a dispersant than was no polymer; however, its molecular weight was quite low.

Solvent

An optimum solvent system probably exists for each useful dispersant polymer. This solvent must solubilize the polymer in the cobalt particle coating sufficiently to allow the particle to grow (by dicobalt octacarbonyl diffusing to the grain surface for decomposition). It should be less polar than the most polar group in the polymer so as not to compete with the polymer in associating with the metal particle. The solvent also, of course, may not chemically react with the metal, polymer, or other components of the system.

The effect of solvent is illustrated by the acrylic dispersant polymers (Table I). Toluene (solubility parameter 8.9¹¹) and chlorobenzene (9.3¹¹) solutions of acrylic terpolymer yields particle chain products of approximately equal magnetic quality. The acrylic copolymer with ten times the *N*-vinyl-2-pyrrolidone polar group content yields particle chains of magnetic quality inferior to the terpolymer in chlorobenzene and fails to yield particle chains in toluene.¹² In this latter case the solvent with higher solubility parameter improves the product, and solvents with still higher parameters may be optimum for this copolymer.

Optimum solubility may be achieved with a solvent below the optimum by adding solvents with solubility parameters above the optimum but which are less polar than the most polar group in the polymer. This is again illustrated by the acrylic terpolymer in Table I. Addition of a small amount of methyl isobutyl ketone to the toluene system leads to a product with magnetic properties better than either the toluene or chlorobenzene system. Thus, the optimum solubility parameter for this polymer system probably lies between 8.9 and 9.3. [Solubility parameter of poly(methyl methacrylate) is 9.0.¹¹]

As a converse illustration, addition of methyl isobutyl ketone to a toluene solution of polychloroprene leads to a product with poorer magnetic prop-

erties. (Solubility parameter of polychloroprene is 8.6.¹¹) In this case, a solvent with a lower solubility parameter than toluene would probably improve the polychloroprene product.

Addition of methyl isobutyl ketone to a toluene solution of polyethyleneoxydiol results in a product with poorer magnetic properties. In this case the ketone is more polar than the hydroxy or ether group and thus decreases the efficiency of the dispersant polymer.

If optimum solvent systems were determined, many of the polymers studied might very well be as good a dispersant polymer as the exhaustively studied acrylic terpolymer.

SUMMARY

To summarize, the preparation of discrete cobalt particles in the 100–1000 Å. range by thermal decomposition of dicobalt octacarbonyl in a polymer solution depends on a very delicate balance between the dispersant polymer, the solvent, and the growing metal particle.

Polymers which have proved to be useful as dispersants are linear addition and condensation products with a backbone made up of relatively nonpolar atoms or molecules. Ideally, more polar groups are attached to the backbone, being separated by at least 100 but no more than 200 backbone atoms. In the lower molecular weight polymers, this spacing and concentration is critical but becomes less important as polymer molecular weight increases.

A thick coating of the polymer on the metal seems desirable for colloid formation and stability. This is achieved by a very high molecular weight such that it is statistically unlikely that the polymer will be totally adsorbed flat on the surface in a thin film or by widely spaced groups along the polymer chain or at its ends which are more polar than the rest of the molecule and are more strongly adsorbed onto the metal surface. These polar groups seem to exclude other parts of the polymer chain and leave it extending from the metal surface in loops or random coils. To date, the best dispersants have been addition polymers with molecular weights in excess of 100,000.

For each dispersant polymer there is an optimum solvent system which must be nonreactive with solution components and should be less polar than the most polar constituent of the polymer.

The authors especially wish to thank Drs. J. R. Thomas and O. H. Harle for their many contributions to this work. They also wish to thank Dr. E. F. Gallegos for his excellent photomicroscopic work, Mr. E. F. Carlston for numerous consultations, and Mr. L. W. Collins for many of the experimental preparations and measurements.

References

1. J. R. Thomas, U.S. Pat. 3,228,881 (January 11, 1966).
2. O. L. Harle and J. R. Thomas, U.S. Pat. 3,228,882 (January 11, 1966).
3. J. R. Thomas, *J. Appl. Phys.*, **37**, 2914 (1966).
4. C. Kittel and J. K. Galt, *Solid State Physics*, **3**, 439 (1956).
5. F. E. Luborsky, *J. Appl. Phys.*, **32**, 1718 (1961).
6. I. S. Jacobs and C. P. Bean, *Phys. Rev.*, **100**, 1060 (1955).

7. A. L. Lyman and F. W. Kavanagh, *Proc. Am. Petrol. Inst., Sec. III*, **39**, 296 (1959).
8. B. J. Fontana and J. R. Thomas, *J. Phys. Chem.*, **65**, 480 (1961).
9. B. J. Fontana, *J. Phys. Chem.*, **67**, 2360 (1963).
10. W. R. Sorenson and T. W. Campbell, *Preparative Methods of Polymer Chemistry*, Interscience, New York, 1961, pp. 168-169.
11. A. V. Tobolsky, *Properties and Structure of Polymers*, Wiley, New York, 1960, pp. 64-66.
12. O. H. Harle, unpublished data.

Résumé

Un processus de préparation de particules de cobalt métallique de grandeur uniforme de 10 à 1000 Å est décrit. On décompose le dicobalt-octacarbonyl en solution en présence de polymères dispersants de façon à former des colloïdes stables de particules discrètes qui sont séparées par leur enveloppe polymérique. La variation de la composition du polymère, du poids moléculaire et du solvant utilisé permet l'obtention de grandeurs particulières différentes et également de différentes stabilités colloïdale. La préparation de particules de cobalt ferro-magnétique avec de bonnes propriétés magnétiques dépend d'une balance très délicate entre le polymère dispersant, le solvant et la particule du métal en croissance. Un grand nombre de polymère d'addition et de condensation peuvent être utilisés comme dispersants. Les plus intéressants sont les polymères d'addition linéaire, de poids moléculaire élevé, ayant une chaîne principale relativement non-polaire. Idéalement, les groupes à polarité plus élevée que la chaîne principale sont attachés à des intervalles d'au moins 100, mais inférieurs à 200 atomes de la chaîne principale. La nécessité de certains groupes plus polaires et leur espacement devient moins critique lorsque le poids moléculaire croît. Les polymères semblent stabiliser les particules métalliques par adsorption à former un film épais qui sépare les particules suffisamment pour maintenir l'énergie d'attraction de van der Waals en-dessous du niveau de l'énergie thermique. Le solvant doit solubiliser l'enveloppe polymérique suffisamment pour permettre à la particule de grandir. Il doit être moins polaire que le groupe le plus polaire du polymère et être chimiquement inerte.

Zusammenfassung

Ein Verfahren zur Herstellung von Kobaltmetallteilchen mit einheitlicher Grösse im Bereich von 10 bis 1000 Å wird beschrieben. Dicobaltoctacarbonyl wird in Lösungen dispergierender Polymerer thermisch zersetzt, wobei sich stabile kolloide Systeme mit diskreten, durch Polymerüberzüge getrennten Teilchen bilden. Eine Variierung der Zusammensetzung und des Molekulargewichts des Polymeren sowie des verwendeten Lösungsmittels führt zu einer Variierung der Teilchengrösse und der Kolloidstabilität. Die Darstellung von ein-domänen-ferromagnetischen Kobaltteilchen mit guten magnetischen Eigenschaften erfordert eine sehr genaue Abstimmung zwischen dem dispergierenden Polymeren, dem Lösungsmittel und dem wachsenden Metallteilchen. Eine Anzahl von Additions- und Kondensationspolymeren kann als Dispersionsmittel verwendet werden. Am besten geeignet sind lineare, hochmolekulare Additions-polymere mit relativ unpolare Hauptkette. Im Idealfall tragen mindestens 100 aber nicht mehr als 200 Hauptkettenatome Gruppen mit grösserer Polarität als die der Hauptkette. Mit zunehmendem Molekulargewicht des Polymeren wird der Bedarf an stärker polaren Gruppen und ihrem Abstand weniger kritisch. Die Polymeren scheinen die Metallteilchen durch Adsorption unter Bildung eines dicken Filmes zu stabilisieren, der eine genügende Trennung der Teilchen herbeiführt, um die van der Waals'sche Anziehungsenergie unterhalb des thermischen Energieniveaus zu halten. Das Lösungsmittel muss eine zur Ermöglichung des Teilchenwachstums ausreichende Solubilisierung des Polymerüberzuges bewirken. Es sollte weniger polar als die am stärksten polare Gruppe im Polymeren und chemisch inert sein.

Received June 27, 1966
Prod. No. 1432