THE PRODUCTION OF FINE PARTICLES USED

IN THE

INVESTIGATION OF FERROMAGNETIC DOMAINS

By

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Bachelor of Arts

Hofstra College

Hempstead, New York

1949

Submitted to the Faculty of the Graduate School of

the Oklahoma Agricultural and Mechanical College

in Partial Fulfillment of the Requirements

for the Degree of
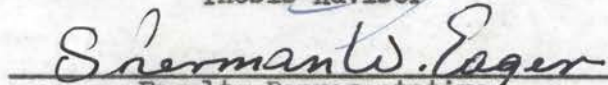
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THESIS AND ABSTRACT APPROVED:

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Preface

The experimental investigation of ferromagnetism is achieved through the observation of the nonhomogeneous magnetic fields existing on the surfaces of crystals of relatively pure ferromagnetic metals. These inhomogeneities are made visible by allowing concentrations of fine ferromagnetic particles to precipitate on the surfaces. In precipitating, the particles form patterns indicative of the crystalline structure and magnetic properties of the metal being investigated.

It is the purpose of this paper to describe various methods of producing concentrations of particles such that desirable patterns will be formed by the precipitates.

The author wishes to express his gratitude to the members of the physics department for their many helpful suggestions. I am especially indebted to R. M. Bozorth of the Bell Telephone Laboratories for supplying many pertinent periodicals and to Dr. Alvin V. Pershing who personally supervised this investigation.

Stillwater, Okla.   Q.C.K.

May 1950

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Chapter I

Theory of Ferromagnetism

Diamagnetism, paramagnetism and ferromagnetism are the three observed phenomena grouped under the general classification of magnetism. The first condition is illustrated by a substance which tends to be repelled by the poles of a magnet, the second by one which is attracted, and the third by one which is attracted very strongly. Commonly observed magnetic effects fall into the latter category for the first two are very weak effects measurable only with intricate apparatus.

The condition known as diamagnetism was first explained with much success by Paul Langevin in 1905. He used classical electrodynamics to formulate a theory based upon the solar system type atom consisting of a positive nucleus as a sun with a negative electron as a planet. The electron revolving in its orbit constituted an electric current and when an external magnetic field was applied an induced magnetic field resulted which opposed the applied field. The result was the diamagnetic effect experienced in the macroscopic state. In order to account for atoms with many electrons, Langevin had to take an average of their orbital radii. Langevin had assumed that there was no interaction between atoms. This eliminates any temperature effects and agrees pretty well with experience for it is found that diamagnetism is little responsive to heat. It is to be noted that all substances are diamagnetic for all atoms are of the type Langevin postulated. Substances which do not show the diamagnetic condition are under the influence of forces stronger than those of this effect.

Since paramagnetism is an effect similar to the orientation and attraction of two bar magnets, Langevin hypothesized that the atoms of substances showing this condition had permanent magnetic moments which were not functions of the applied field as in the case of diamagnetism. He attributed this moment to odd electrons in unclosed electronic shells. Any electron in a closed shell would have its moment opposed by another electron in the shell. The total effect for a closed shell would be a cancellation of any external moment. For an odd electron in an unclosed shell there would be a net external moment. The orientation of this moment in an applied field leads to the macroscopic paramagnetic condition. If the permanent magnetic moment of such an atom is stronger than the induced moment due to the applied field the net result will be paramagnetism. Since the orientation of the atoms is what produces the observed condition we find that the temperature has a decided effect. To account for this Langevin used statistical theory, assuming that the permanent moment of an atom could be oriented in any direction. Here again no interatomic interaction was permitted.

In 1907 Pierre Weiss extended Langevin's theory to include the ferromagnetic effect. He did this by postulating that the atomic magnetic moment was not only subject to the applied field but also to a 'molecular field' dependent upon the degree of magnetization. In effect the new field strengthened the applied field. It is to be noted that the molecular field experienced by any atom resulted from the combined effect of the other atoms in the mass. Sir James Ewing had previously attempted a theoretical description of ferromagnetism based upon interatomic forces but was unable to correlate his findings with experience. Weiss did not at-

tempt to show the origin of his newly conceived field; he postulated it. In this way he was able to avoid the specific derivation of the field and to utilize the new concept to correlate known theory with ferromagnetic phenomena.

R. M. Bozorth shows this very nicely by adding Weiss's field to Langevin's equation for paramagnetism. "The resulting equation is perhaps the most important in the theory of ferromagnetism."[1] The equation shows that magnetization still exists even when the applied field is zero. When proper substitutions are made it is shown that for all temperatures below the Curie point a definite value of magnetization should be realized.[2] As it is quite obvious that iron is not magnetized under these conditions Weiss further postulated the domain theory. The domain theory assumes that a substance is composed of increment volumes called domains which have the saturated degree of magnetization predicted by the theory. The reason that no macroscopic magnetization is observed is a result of the fact that the domains are completely disoriented under normal conditions in the metal.

Weiss's molecular field assumption made such a good correlation with previous theory and observed phenomena that its specific derivation was very much desired. W. Heisenberg in 1928 was the first to propose an explanation. Using the Heitler-London atom model where it is assumed that the electrons responsible for ferromagnetism remain in the same atom, he was able to show the existence of a quantum mechanical force different

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[1] R. M. Bozorth, Rev. of Mod. Phys., Vol. 19, p. 73, 1947.

[2] Bozorth, loc. cit.

from the classical forces of magnetism and electrostatics. Unlike the
latter two, this force does not obey the inverse square law. H. Bethe
and J. C. Slater supposed this force to be maximum at a certain critical
distance. The effect of the force is to orient electron spin magnetic
moments of interacting atoms in some definite direction. As the distance
between atoms is extended beyond the critical point, the force reduces to
zero and as it is decreased from the optimum, the force not only decreases
but becomes negative causing the spin moments of adjacent atoms to cancel
each other. It is assumed that the interatomic distance is twice the
radius of the atom. With this assumption we consider the ratio of the
atomic radius to the radius of the shell possessing the electrons causing
the ferromagnetic effect. A result of Slater's work is that this ratio
reaches a maximum for the ferromagnetic metals. What this means is that
the interatomic distance for the ferromagnetic metals is such that the
Heisenberg quantum mechanical force is a maximum.

F. Bloch and E. C. Stoner approached the problem of ferromagnetism
through the use of the Hund-Mulliken model of the atom which supposes that
the electrons responsible for ferromagnetism may circulate from one atom
to another. This method does not account for Weiss's postulated field but
the theory is substantiated by certain experimental evidence. In effect,
what we have in this theory are many 'valence' electrons. These are the
eight 3d and 4s electrons of iron, say. When the electrons are considered
as moving in the nonhomogeneous potential field formed by the atomic nu-
clei, the quantum mechanical approach shows that only certain permissible
energy ranges are allowed. These ranges are called bands and we may think
of a band representing the possible energy ranges of the 3d electrons with
positive spins and another the 3d electrons with negative spins. The con-

dition of ferromagnetism is a result of certain relations existing between the two bands. Theory predicts an atomic magnetic moment for iron of 2.6 Bohr magnetons whereas the measured value is 2.2. F. Seitz[3], writing in 1943, states that until then no reason could be given for the discrepancy. The experimental evidence with which the band theory agrees very closely arises from the alloying of nickle and copper. Nickle is ferromagnetic because its positive band has an excess of electrons over the negative. If copper is alloyed with nickle the extra valence electrons of the copper fill up the positive band in the nickle and destroy the condition for ferromagnetism.

Both theories give satisfactory explanations of ferromagnetism but they do not agree exactly with observed phenomena. J. H. Van Vleck[4] gives a comparison of the two systems but feels that the final answer will lie somewhere between the two. He mentions that the intermediate case will be too difficult to calculate but that on the whole the quantum mechanical approach gives a satisfactory explanation of ferromagnetism. He expresses his belief in the following words:[5]

"If...what one desires of a theory is a qualitative understanding of why nature works as it does, and the satisfying confidence of having a mechanism which would...explain even the most complicated phenomena if the difficult mathematical calculations could be made, then the quantum theory of ferromagnetism...is certainly a success."

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[3] F. Seitz, The Physics of Metals, p. 309, 1943.

[4] J. H. Van Vleck, Rev. of Mod. Phys., Vol. 17, pp. 37, 40-43, 1945.

[5] Ibid., p.47.

Weiss's domain postulate has not received as much praise as his molecular field theory. That domains exist is evidenced by actual observation but there has been some difficulty in correlating the different domain phenomena. The hysteresis curve, F. Bitter's powder patterns and the Barkhausen effect are the best known experimental evidences of domains. The domains associated with each phenomenon are assumed to have different qualities when the individual mathematical explanations of the observations are given. Even though F. Zwicky[6] was able to give an account of the observed hexagonal powder patterns of cobalt in terms of his cooperative phenomena, W. F. Brown, Jr.[7] in 1945 made the statement that, "...detailed calculations and analyses based on it (domain theory) are of doubtful value".

Nonetheless, considerable work has been done, especially in the field of powder patterns. Ever since Bitter (1931) introduced the concept of the possibility of observing Weiss's domains because of the inhomogeneities in the magnetic field resulting from the domains, important advances have been made. Probably the most spectacular was made when L. Neel using a theory of domain structure associated with least energy predicted the existence of certain patterns which were observed at a later date.[8]

The general idea of Bitter's work was to apply concentrations of small magnetic particles on the surfaces of ferromagnetic materials. The particles

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[6] F. Zwicky, Phys. Rev., Vol. 43, p. 277, 1933.

[7] W. F. Brown, Jr., Rev. of Mod. Phys., Vol. 17, p. 18, 1945.

[8] H. J. Williams, R. M. Bozorth, and W. Shockley, Phys. Rev., Vol. 75, p. 170, 1949.

have a tendency to precipitate out of the medium at those places where the magnetic leakage from the individual domains is the greatest. The effect is an observable geometric pattern which on single crystals of relatively pure metals bears a definite relationship to the actual domain structure. Domains are not necessarily microscopic entities for some have been observed with dimensions greater than one centimeter.[9]

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[9] H. J. Williams and W. Shockley, _Phys. Rev._, Vol. 75, p. 178, 1949.

Chapter II

Experimental Procedure

When the author began this investigation his adviser, Dr. Alvin V. Pershing, had already done some preliminary work. This consisted of mortar and pestle grinding of commercially available iron filings (Fig.1) and Fe_2O_3 (jeweller's rouge) in water (Fig. 2) and the observation of domain and crystalline structure on the polished polepiece of a large alnico 5, horseshoe magnet supplied by the Central Scientific Company (cat. no. 78329, 5"x5") (Fig. 3).

It was decided at one of the preliminary discussions that the object of the investigation would be a study of methods of production of fine particles which would yield satisfactory powder patterns. To assure proper comparison of the ability of different materials to form patterns, it was further agreed that the polished pole of the above-mentioned magnet would be used as a standard (Figs. 4 and 5).

Since it was obvious that the desired result was the procurement of very small ferromagnetic particles, the author first put to use a concept recalled from previous reading. This was the production of colloidal iron particles by passage of a high voltage arc between iron terminals. A demonstration type induction coil was used with its high voltage terminals connected to two iron nails thrust through corks in the ends of a 'T' tube. The 'T' was held in an inverted position and the horizontal bar with the electrodes was filled with liquid which was to act as a medium for the colloid. Kerosene and carbon tetrachloride were used but both these broke down under the arc. It was felt that there would be no
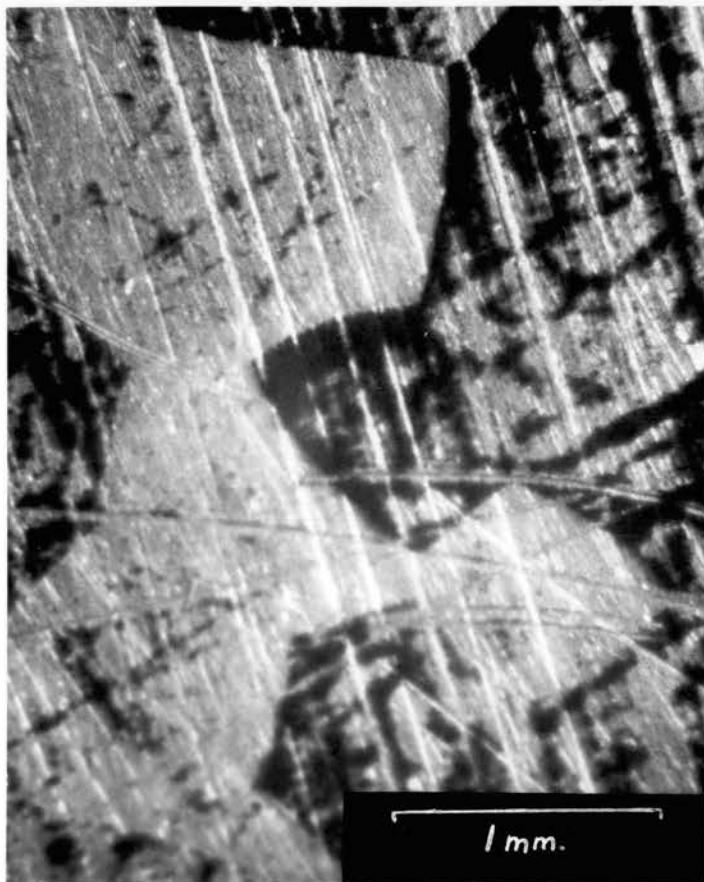
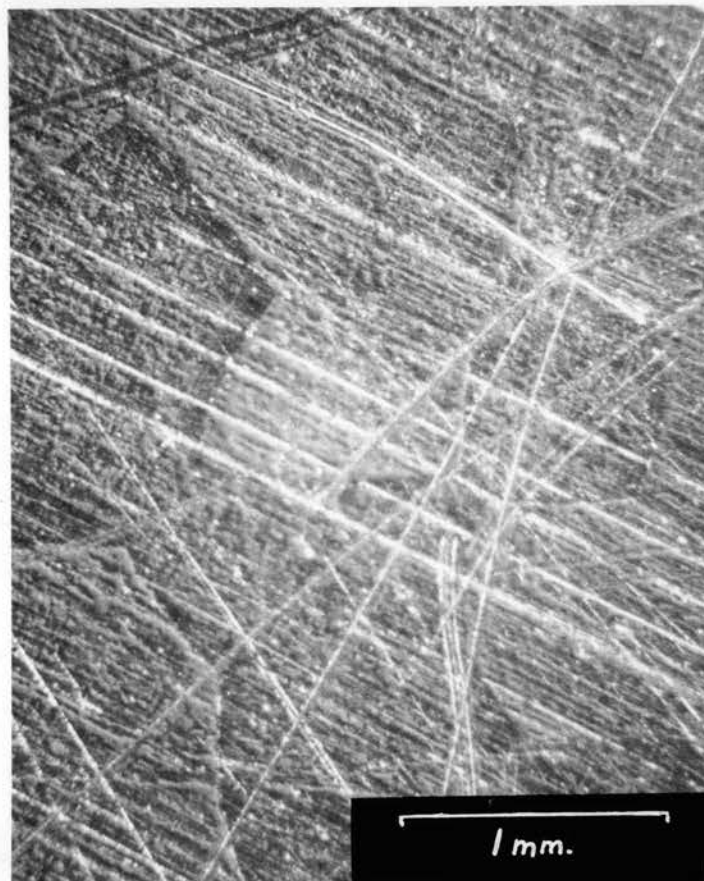Fig. 1. Iron filings ground in mortar (35X).

Fig. 2. Jeweller's rouge ground in mortar (35X).

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Fig. 3. The two magnets used as sources of
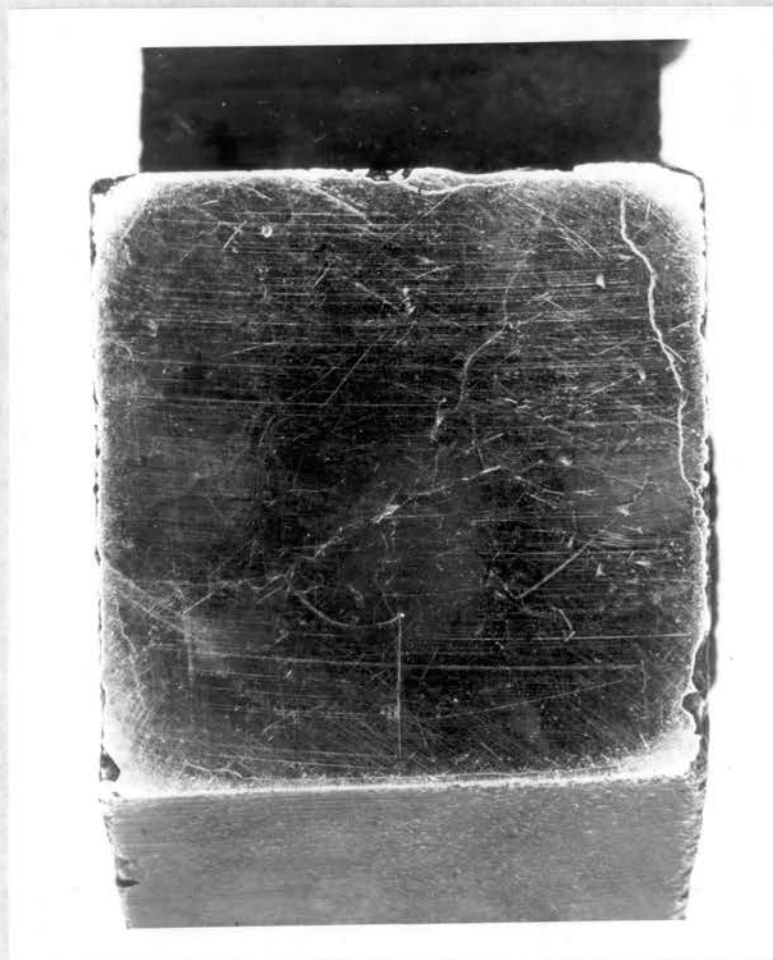patterns for this investigation.

Fig. 4. Surface of magnet (2X).

Fig. 5. Surface of magnet with particles (2X).

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purpose in using water as a vehicle for the fine particles of iron would rapidly combine with the dissolved oxygen. Since the net result of this experiment was a collection of partially oxidized liquids with no noticeable yield of magnetic particles the method was no longer considered as a possible source of particles.

The author then felt that the best method of determining the approximate size the particles should attain would be to repeat the previous work of Dr. Pershing. Small amounts of iron and Fe_2O_3 were ground separately in a 25 ml. mortar with water. As had been experienced, this method yielded particles which immediately upon application to the magnet's pole formed patterns indicative of the subsurface structure. These particles were nowhere near colloidal for they were readily visible in the microscope at low power. At this point the detrimental effect of the use of water as a medium became apparent. If the medium was not removed after making the observation of the pattern it was discovered that the water combined with the metal of the magnet. This caused the polished surface to become stained and frequent polishing was necessary. This polishing was done with a soft cloth and jeweller's rouge combined with a little water. It was decided to try mineral oil as a medium to hold the particles.

Ordinary medicinal mineral oil was purchased and the preliminary trials made with this. It was immediately observed that the oil was much too viscous to permit the rapid formation of a pattern. Carbon tetrachloride was used to reduce the viscosity but was found to be unsuited because of its extremely high rate of evaporation. The motion of the particles resulting from the evaporation was so great that no pattern could form on the surface. It was observed, however, that the subsurface

structure of the magnet could be seen in the mass of 'boiling' particles in the space above the surface of the pole. This last condition was observed with particles of FeS. This experiment showed that it would be necessary to find some other medium with which to reduce the viscosity of the mineral oil to a point that would permit the rapid precipitation of the suspended particles. It would be a further necessity that this solvent have a low rate of evaporation.

Instead of following the above-mentioned trend it was decided to first try something mentioned by McKeehan and Elmore[1]. They had used a true sol (a 'sol' is a colloidal suspension of a solid in a liquid) of Fe_2O_3 in water mixed with a little KOH. No mention of the method of preparation was given. An attempt at its preparation was made by grinding some of the ferric oxide in the 25 ml. mortar with water to which a little NaOH had been added. There was no noticeable difference between this and the previous trial without the sodium hydroxide. Apparently some less obvious method had been used to obtain the sol.

A visit to the local physical chemistry department resulted in the procurement of a sample of dialyzed ferric oxide. This is a brown transparent sol with particles too small to be seen with the high power (400X) of the microscope available. Some of this liquid was applied to the surface of the magnet and no pattern was produced. The liquid was allowed to remain overnight and the following morning there was a stain on the surface. The peculiar thing about the stain was that it showed the same pattern as previously seen on the magnet. The conclusion reached was that

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[1] W. L. McKeehan & W. C. Elmore, Phys. Rev., Vol. 46, p. 226, 1934.

the particles in the colloid were too small to precipitate out but were able to show the pattern when the liquid had evaporated. This, in combination with the previously experienced stain, had produced the observed phenomenon. The obvious result of this experiment was that the particles can be too small to be of any use. This was later found to be substantiated by Elmore[2] who suggested that the particles should be in the upper range of colloid sizes.

At this point it was decided to return to the problem of finding an oil of the proper viscosity. There happened to be a can of 3-in-1 oil in the laboratory and as this seemed of much lower viscosity than the mineral oil it was tried as a medium. It worked very well but there was still a noticeable tendency for the liquid to slow down the precipitation of the particles. The trend seemed to indicate that only the thinnest of oils would be found to be satisfactory. The best known example of an oil with low viscosity and low rate of evaporation is kerosene and this was the next liquid put to the test. Kerosene was found to be entirely satisfactory. It not only satisfied the conditions of low viscosity and rate of evaporation but it was also colorless. This was another advantage over the 3-in-1 oil which was available. The latter had a definite yellow color.

The next important step in the investigation was the discovery of Elmore's[3] recipe for the production of colloidal magnetite (Fe_3O_4). His instructions were as follows: Dissolve 2.0 gr. $FeCl_2 \cdot 4\ H_2O$ and 5.4 gr. $FeCl_3 \cdot 6\ H_2O$ (or the equivalent amount of sulphates) in 300 cc. hot water and add with constant stirring 5.0 gr. NaOH previously dissolved in

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[2] W. C. Elmore, Phys. Rev., Vol. 54, p. 309, 1938.

[3] Ibid., p. 310.

50 cc. of water. Filter to remove salt and excess NaOH. Rinse precipitate in filter several times with water and finally once with 0.01 N.HCl. Transfer precipitate to one liter of 0.5% soap solution and boil for short time. The former precipitate will now become colloidal except for part which must be filtered while hot. A drop or two of solution is all that is needed to observe patterns. Williams, Bozorth and Shockley[4] made a more concentrated solution by using only 100 cc. of the soap solution.

After one failure the author was able to duplicate Elmore's colloid. It yielded excellent patterns, these being the finest seen up to that time (Fig. 6). The precipitated particles actually produced a lace-like design in conforming to the surface fields. Previously it had always been possible to see the individual particles but in using the new colloid it was noticed that the pattern seemed to appear out of the solution. The single particles were not visible. This was true even at 400X magnification.

The Bozorth modification was also tried. As before, the first attempt resulted in failure but the second try produced an entirely satisfactory colloid. In using this solution it was noticed that the naked eye patterns were much more intense but there was a tendency for the more concentrated colloid to precipitate too many particles. The result was a smothering of the more delicate features in 'piles' of magnetite (Fig. 7).

The author made one major change in the procedure of producing colloids such as these. Because no method was available for forcing the

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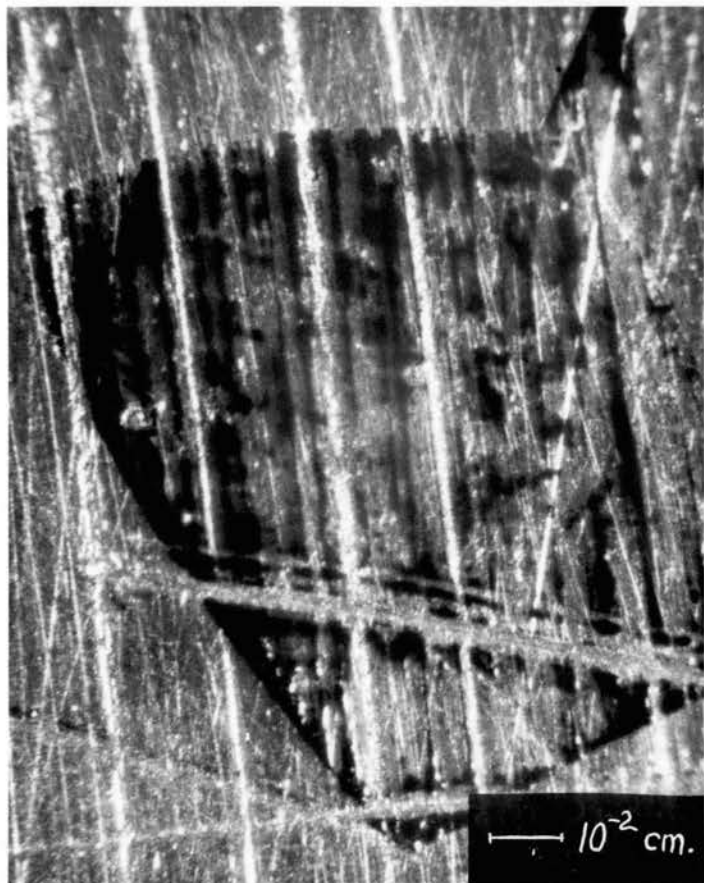[4] H. J. Williams, R. M. Bozorth, and W. Shockley, Phys. Rev., Vol. 75, 1949.

Fig. 6. Elmore's colloid - Fe_3O_4 (100X).

Fig. 7. Concentrated colloid showing piles of magnetite (100X).

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liquids through the filter and since many such steps are included in the process it was decided that the precipitate could be washed by rinsing rather than by filtering. The precipitate was permitted to settle and the liquid was then removed by pouring it off the top. Fresh water was added and the process was repeated. The final addition was the weak acid solution. This change may have been the primary reason for the two failures already mentioned.

It is pertinent to mention at this time that both the colloids are susceptible to putrefaction. In the case of the less concentrated one definite mold formations were observed after the solution had been standing in the laboratory for a few days. Along with this was a 'mother of vinegar' type of structure which ruined the solution for further use with the microscope. Long strands of organic material were visible and the liquid itself took on a drab brown color in contrast to its previous black. The more concentrated solution has been found more stable but this may be due to the different soap used. It is to be noted that no mention is made by Elmore as to the type of soap to use in the preparation of the colloid. In the case of the first failure the author had used ordinary liquid hand soap from the lavatory and at the onset it was thought that this was the cause of the failure. Dry castile soap was used in the second attempt. It just so happens that in making the more concentrated solution castile soap was used in the failure and hand soap in the attempt that was successful. Since the soap is the only ingredient that would appear to be able to support life it is assumed that the castile soap is more prone to putrefaction than that supplied for hand use. In a later

article, Elmore[5] mentions that he experienced a chemical deterioration of the sol. This apparently accounts for the color change from the deep black to the muddy brown.

In order to understand the method of colloid production used by Elmore the author turned to the texts of physical chemistry. Although there is an extensive literature pertaining to colloids most of the articles refer to the production of extremely small particles in low concentrations. This was of little use in this investigation for, as already mentioned, it is quite possible to have particles too small to form the desired patterns. Certain definitions and other generalities were of use, however. Pertinent definitions follow:

Colloid - a mixture containing small particles of the order of 10^{-5} to 10^{-7} cm. The particles are invisible optically but do not form a molecular solution for they do not pass through membranes.

Sol - a colloid formed by solid particles in a liquid medium.

Hydrophobic - pertaining to a sol the particles of which have an aversion for the liquid medium used - not gelatinous.

Hydrophilic - pertaining to a sol the particles of which have an affinity for the liquid medium used - gelatinous.

Peptizing - the process whereby relatively large particles are changed to smaller ones.

Protecting - the process of coating peptized particles to prevent them from coagulating back to their original state.

These definitions will be used to explain the process used by Elmore in forming his colloid.

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[5] W. C. Elmore, Phys. Rev., Vol. 62, p. 486, 1942.

First the substance whose sol we want is precipitated by chemical means. The rinsing steps are just a means of obtaining a pure form of the substance (in this case Fe_3O_4). The iron oxide is then peptized with the weak HCl after which it is protected by the soap solution. The boiling in the final step is to assure proper dispersion of the fine particles. The filtering removes any particles which were not dispersed by the boiling.

Once this general process was known it was decided to attempt the production of colloids using other compounds of ferromagnetic elements. The trials were made with various compounds selected because of their insolubility in water. In this way it was possible to compare the process with that used by Elmore. The precipitates used were:

$Fe_3(PO_4)_2$	ferrous orthophosphate
$Fe(OH)_2$	ferrous hydroxide
$Fe(OH)_3$	ferric hydroxide
FeS	ferrous sulfide
$Fe_2Fe(CN)_6$	ferrous ferrocyanide
$Fe_4(Fe(CN)_6)_3$	ferric ferrocyanide
$Fe(P_2O_7)$	ferrous pyrophosphate
$Fe_2(P_2O_7)$	ferric pyrophosphate

None of these formed colloids of the Elmore type. Some became partially colloidal but the particles were extremely small and did not yield any pattern when precipitated on the surface of the magnet. Since most of the compounds consisted of particles large enough for the filter to retain there was a large amount of filtrate left from these trials. These were permitted to dry and retained for future use. It is to be noted that the ferrous compounds were rapidly reduced to the ferric state by exposure

to the air. This resulted in a collection of dried chemicals the exact formulation of which was unknown.

No reason can be given for these failures just as none is known for the failure of the first trials of the Elmore and Bozorth colloids. To eliminate errors due to impurities the following precautions were taken:

Distilled water was used for all solutions and rinses;

Dried castile soap was used in order to have a known standard.

Somewhat later in the investigation the Elmore method was tried again. Since Fe_3O_4 happens to be a hydrophobic substance it was thought that the process might only work on similar compounds. The following hydrophobic compounds were used in these trials:

$Fe_4(Fe(CN)_6)_3$ ferric ferrocyanide

FeO   ferrous oxide

In these attempts some success in making colloids was experienced but the results were of little value as far as the investigation is concerned. The ferric ferrocyanide became colloidal in a manner similar to Elmore's Fe_3O_4. Most of the precipitate was peptized to the point where it would pass through the filter. The trouble with this compound was that it was not magnetic enough to cause the particles to precipitate from the suspension or perhaps the particles were too small. This resulted in no formation of patterns. The ferrous oxide did not form a colloid at all.

Since the only success experienced with the chemical production of colloids was the preparation of the one suggested by the literature, it was decided that the next line of endeavor would be to return to the use of hand grinding methods.

In previous grinding it had been noticed that the finer particles remained in suspension for a much longer period than the larger. This was used as a method of separation. After the compound had been ground in liquid, the suspension was permitted to stand and then only the upper portion of the liquid was decanted. The compound was then subjected to a further grinding after which more liquid was added. The liquid was thoroughly mixed with the compound and the above decanting process repeated. This method was found to work with commercially available iron (Genco F-2573-B iron filings), iron sulfide (Fig. 8) and iron oxide (Fe_2O_3) in its two forms, jeweller's rouge and ordinary rust. Figures 19 and 21 through 24 are various patterns obtained using ordinary rust scraped from a weathered iron pipe. The dry rust was first subjected to a strong magnetic field to remove any particles of iron. After this separation the rust was ground using the general method described below. The method did not work well with commercially prepared Fe_3O_4, nickle powder or $FeSO_4$ (Fig. 9). Note the large grain size in the latter figure.

Grinding Method

Use 100 ml. mortar (output was greater with larger mortar).

Use 30 cc. kerosene and 2 cc. of desired compound.

Grind the above mixture for about one minute. It will be found that the grinding produces a cloudlike mixture composed of particles of all sizes. Remove the pestle and wait until it is possible to see the surface of the powder layer below the surface of the liquid. Pour off the liquid without disturbing the bottom layer of powder. It will be found that the liquid contains many small particles while the heavier ones have precipitated to the bottom layer. Add more kerosene after grinding the powder a second time. Mix the kerosene thoroughly with the powder and decant as before. The yield of small particles increases with each step. This is only a temporary condition, however, for later on the yield drops off and it is more profitable to restart the entire process with a new supply of compound.
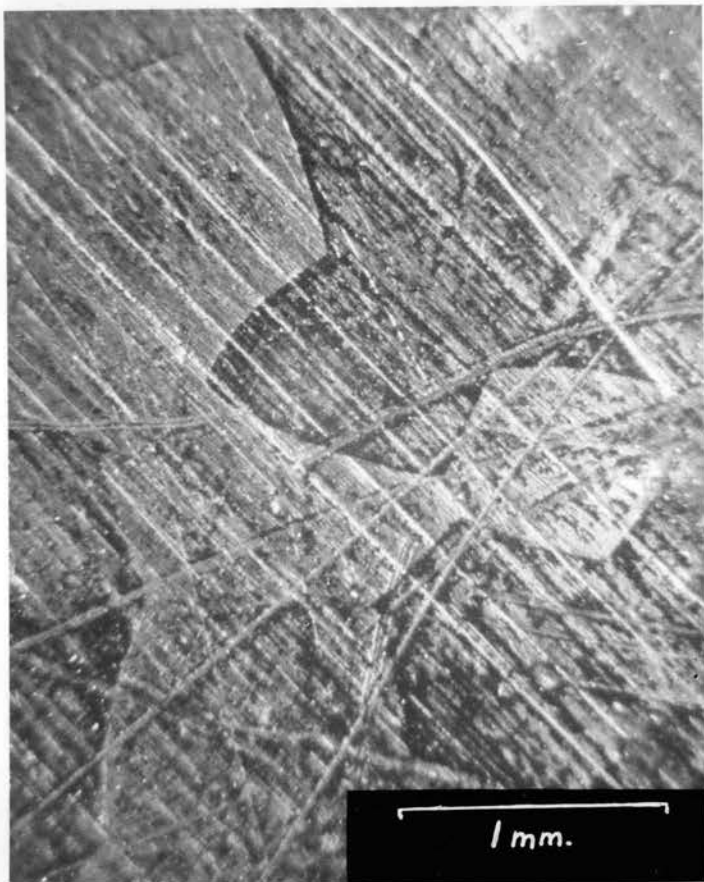
Fig. 8. Ferrous sulfide ground in
mortar with kerosene (35X).

Fig. 9. Ferrous sulfate ground in mortar
with kerosene. Note large particles
(100X).

When this process was tried with the first three compounds mentioned above a very satisfactory yield resulted. In the case of the iron 20 grams of filings yielded nearly one full gram of fine particles with less than one half hour of grinding. When you consider that this gram will make about 100 ml. of pattern-forming mixture and that only one drop is used at a time, it can be seen that the process is quite satisfactory. Why the yield is nearly zero with the other three substances mentioned is not known. After even longer periods of grinding it was found that the particles precipitated quickly and none were small enough to be supported by the liquid.

One addition should be made in the above method when strongly ferromagnetic substances are used. It was found that the larger particles could be precipitated much more rapidly than with gravity alone if the clouded mixture was put in a strong magnetic field. Immediately after grinding the entire mortar was placed upon the pole of the same magnet used for observation. It was found that there was practically an immediate precipitation of the larger particles. If the liquid was decanted while the mortar was in this position the magnetic field securely fastened the unwanted powder layer to the bottom of the mortar and the process of decanting was hastened considerably. After a sufficient amount of fine particles is obtained by this method the mixture of fine particles should be thoroughly shaken and placed in test tubes. If the magnetic separation process is carried out again by pouring the mixture from one test tube held over the magnet into another test tube, there is good assurance that no large particles will be left for the magnetic field keeps them in the first tube.

The next method of producing fine particles combines the grinding

and chemical processes described previously. This is a new procedure
which was discovered when the grinding method was applied to the dried
filtrates remaining from the colloid failures. It should be remem-
bered that these filtrates were originally subjected to the processes
of peptization and protection. Apparently the particles formed were
not small enough to pass through the filter but some action had taken
place for no sooner had the grinding started when it was noticed that
the cloudy mixture was much more dense than had been previously ex-
perienced. In fact, it was soon discovered that the mixture never
settled. The grinding process seemed to be the necessary step which
completed the process begun by the peptizing and protecting. Since
Fe_3O_4 is quite ferromagnetic the magnetic separation process was used
on the ground Elmore failure to eliminate the larger particles. The
mixture that was left consisted of the small particles not precipitated
by the magnet together with a true sol which showed the Tyndall effect
under strong illumination. The mixture was permitted to stand for an
hour or two and this time was found sufficient to permit the precipita-
tion of the smaller particles which formed very nice patterns with a-
bout the same definition as the original Elmore colloid. The remaining
colloid would permit no noticeable precipitation over a period of a
few hours but when permitted to stand for several days it did yield a
very fine precipitate. Once this had been collected by careful decant-
ing there was no precipitation even after a period of a month or two.
The true sol remaining did not form patterns except in the extreme case
when a relatively large amount was placed upon the magnet and left there
until the medium had evaporated. The resulting pattern showed very
little detail for it amounted to little more then a faint discoloration

Fig. 10. True sol boiled to form precipitate (100X).

Fig. 11. Pattern due to $CoCO_3$ (100X).

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of the surface of the magnet.

Since the evaporation of the kerosene had left a pattern of sorts, the idea of attempting to concentrate the sol in hopes of obtaining a sufficient quantity of small particles to cause a rapid precipitation came to mind. No still was available but an attempt was made to boil off some of the kerosene from a test tube filled with the sol. Instead of the liquid remaining a sol, the boiling process caused the precipitation of the colloid particles. When this precipitate had been collected and applied to the surface of the magnet it was discovered that very lacelike patterns were formed (Fig. 10). These particles were nearly of the colloidal size for when the mixture was vigorously shaken it took a considerable amount of time before the particles finally settled.

The fact that the Elmore failures had responded so well to the grinding method led to further investigation. Since the dried precipitates had been subjected to the peptizing and protecting processes it was decided to see which of these two steps had the greater effect. Fresh precipitates of nickel hydroxide and ferrous oxide were formed. These were divided into three equal quantities. One group was peptized with acid, one was protected with soap and the other was given both treatments. The masses were then dried and ground in the usual manner. The results for the nickel hydroxide are shown in Figures 12-14 and for the ferrous oxide in Figures 15-17. In the latter case there is no noticeable difference in the photographs. To the naked eye, however, there was a marked abundance of large particles in the specimen given only the acid peptizing. The grain size of the nickel hydroxide is quite noticeably larger in the batch given the same treatment. The increase in particle size seems to be due more to coagulation than to the existence of larger

particles. Without the protecting soap the small grains adhere to each other and give the impression of large size. As a check of the power of the protecting process rust was boiled in soap water and then ground. The result was a near colloid which formed very delicate patterns as shown in Fig. 25.

During the course of this investigation the possibility of producing colloids through the use of ultrasonic radiations was suggested. Since it is well known that high frequency longitudinal waves have the power to homogenize normally immiscible liquids the idea seemed a sound one. A cursory investigation of the literature indicated that ultrasonic waves had the power to peptize small particles[6]. No specific instructions were found, however. It was decided to attempt the production of colloids by this method. Permission was obtained to use the ultrasonic generator from Dr. Sherman W. Eager. The generator was of the very low radio frequency crystal oscillator type.

A copper can with a thin diaphragm of brass at the bottom was used as a container. This device had previously been used to homogenize water and benzene. A frequency of 450 KC. was used at a plate power input of one hundred watts. The idea of this experiment was to form the desired compounds by chemical precipitation while the water medium was being radiated by ultrasonic waves. It was hoped that the radiation would separate the particles formed and a colloid would result. Two trials were run. One with Fe_3O_4 and the other with FeO. The copper can was placed in the oil disturbed by the vibrations of the crystal. The soluble iron salts were placed in the tube and irradiated. Then the hydroxide was

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[6] K. Sollner, Trans. Faraday Soc., Vol. 34, p. 1171, 1938.

Fig. 12. $N_1(OH)_2$ peptized with acid (100X).

Fig. 13. $N_1(OH)_2$ peptized with acid and protected with soap (100X).

Fig. 14. Ni(OH)$_2$ protected with soap (100X).

Fig. 15. FeO protected with soap (100X).

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Fig. 16. FeO peptized with acid (100X).

Fig. 17. FeO peptized with acid and
protected with soap (100X).

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added to form the oxide. Instead of dispersing the particles it was found that ultrasonic waves had coagulated the newly formed precipitate. The result was the production of a few large lumps of waterlogged iron oxide. The ultrasonic radiation had an effect just the opposite of what had been hoped it would do.

When it was realized that every compound that had been tried had shown some tendency to form a pattern it was decided to investigate further. Many compounds of iron, nickel and cobalt were formed and these were tested on the surface of the magnet to see if they would produce a pattern. This was done without grinding for in the original water solutions the particles were rather small. It was found necessary to thoroughly clean the surface of the magnet to remove all traces of kerosene before any observations could be made. Before this was done the water solutions formed globules which were too thick to permit visibility through the microscope. A pattern due to a cobalt compound is shown in Fig. 11. Besides the above mentioned compounds it was also decided to try to find a pattern when antimony was used. Since the diamagnetic condition is a relatively weak one no pattern was observed in this case.

Attention is called to the comparisons represented by Figures 18 and 19 and Figures 20 and 21. In the former two the pattern due to the surface scratches may be readily compared with these features. The picture with the powder applied (Fig. 19) clearly shows the magnetic inhomogenieties of the surface. The major ones are shown by the heavy line of particles and the somewhat parallel line to the left upon which no rust is deposited. The latter two illustrations show a similar condition but the pattern seems to be due to the crystalline structure of the magnet.

Fig. 18. Magnet's surface before particles
are applied. Compare with Fig. 19.

Fig. 19. Magnet's surface after particles
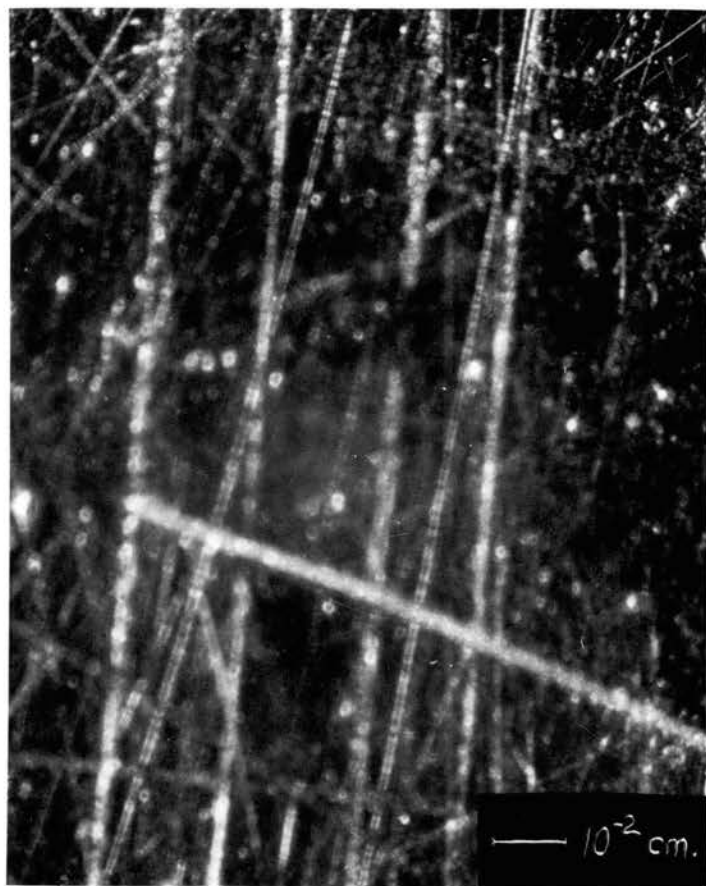are applied. Compare with Fig. 18.

32

Fig. 20. Magnet's surface before particles
are applied. Compare with Fig. 21.

Fig. 21. Magnet's surface after particles
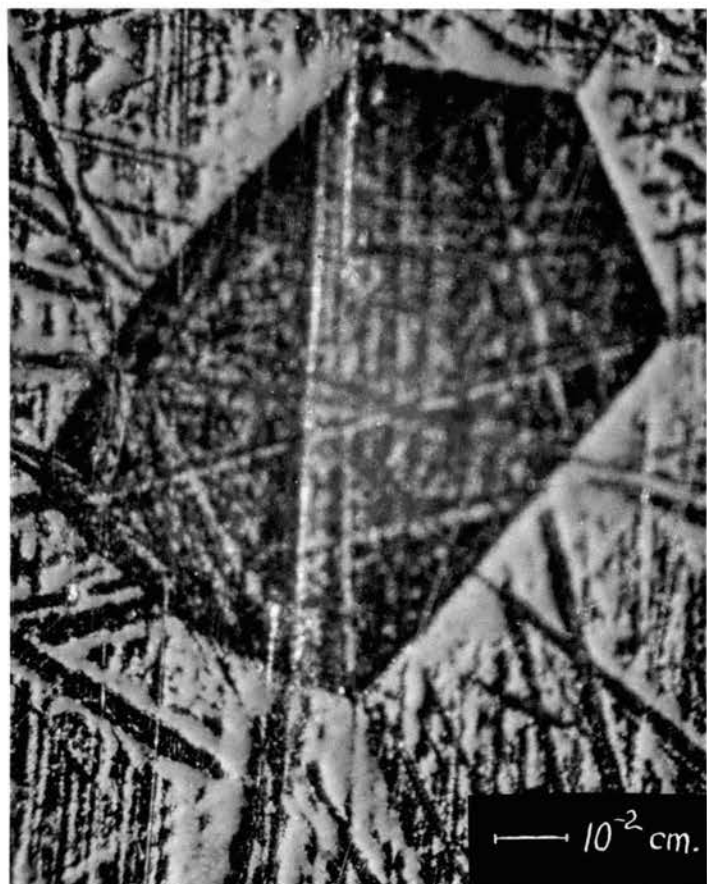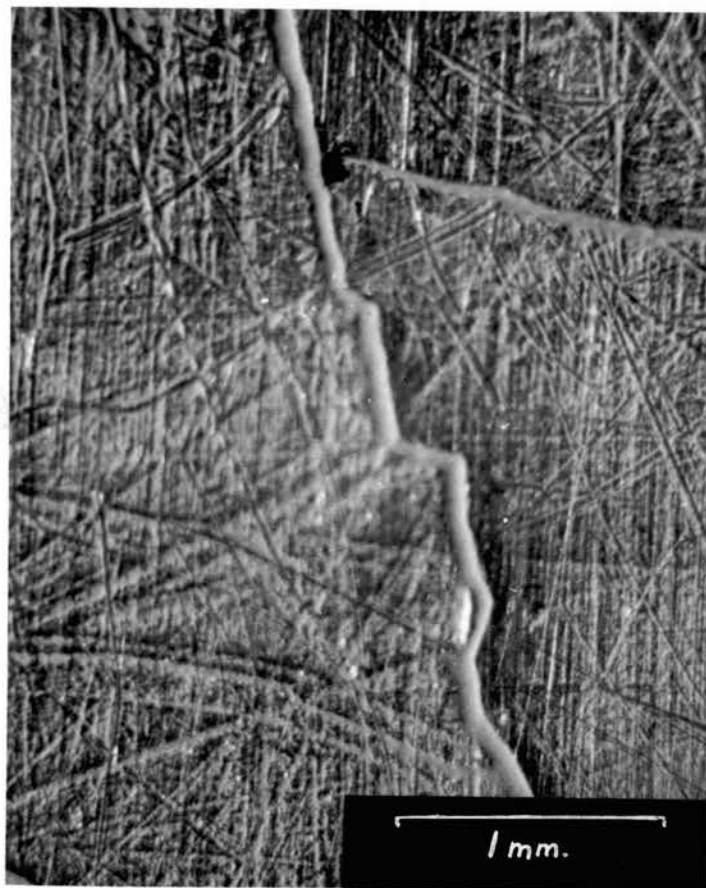are applied. Compare with Fig. 20.

33

Fig. 22. Rust pattern.

Fig. 23. Rust pattern resulting
from surface fissure.

Fig. 24. Hexagonal pattern formed by rust
            (approx. 80X).

Fig. 25. Hexagonal pattern formed by rust
            (approx. 80X).

Chapter III

Photographic Methods

When an optical system is arranged so that the emergent rays are parallel, the image has an effective distance of infinity. This is the basic rule behind the method used to obtain the photomicrographs included in this thesis. Since the eye is focused at infinity when it is at ease, the microscope was focused with the eye relaxed in order that the emergent rays be parallel. To get a picture of the image it was only necessary to set the camera's focusing scale at infinity and put it in the position normally occupied by the eye. When this process was carried out it was found to work very well.

Some trouble was experienced with the particular microscope used. It happened to be a Carl Zeiss student model with extremely noticeable curvature of field. The defect was readily apparent for it was possible to focus first on the center of the field and then change the focus to the edges. Another annoyance was the inability of the instrument to maintain its focused position. The lens tube moved relative to the base under the action of gravity. This was partially corrected by increasing the friction between the two parts but there was no real assurance that proper focus would be obtained when any single exposure was made. The curvature is discernible in Fig. 20 where the center is out of focus while the top is not.

The microscope had a 10X eyepiece and objectives of 3, 8, and 40 power which permitted magnifications of 30, 80 and 400 times. It was found by experiment that the exit pupil of the microscope was smaller

Fig. 26. Foth Derby camera in picture
taking position on Zeiss microscope.

than the smallest diaphragm stop so all exposures were constant in respect to the camera's diaphragm setting.

Two cameras were used. These were:

1. Foth Derby #127 roll film miniature with f/3.5 three element lens of 2" f. l. Picture size - 3 X 4 cm.

2. Ernemann double extension cut film type with f/6.3 three element lens of 6" f. l. Picture size - $3\frac{1}{4}$ X $4\frac{3}{4}$ inches.

When photomicrographs were taken, a black paper cylinder was taped to the camera and the camera was rested on the eyepiece of the microscope (Fig. 26). In the case of the Ernemann it was found that a counter balance was necessary. It was also found that the infinity focusing method cut off part of the circular field when the Ernemann was used. This was corrected by ground glass focusing with the lens-to-film distance set at about four inches.

Eastman Plus-X panchromatic roll film was used in the Foth Derby and Superpanchro-Press type B was used in the Ernemann.

At first all negative material was developed in Eastman DK60a but this was found to be far too grainy for the miniature size. The grain size was considerably reduced by using FR X-33 fine grain developer.

When the substage mirror was used in photographing particles it was found that the illumination from the 100 watt lamp was far too intense. This was remedied by varying the voltage applied to the lamp with a variable autotransformer (Variac). Exposures of five seconds yielded fine negatives when 20 volts was used at 30X, 30 volts at 80X, and 50 volts at 400X. These are, of course, only approximations. The bright spot seen in the photographs taken at 400X magnification (Figs. 27, 31 and 32) seems to be a defect in the optical system. The spot appeared on all negatives where this degree of magnification was used and no arrangement

of the light source could be found wherein the spot was not visible.

Eastman Kodabromide was used for the prints. Glossy surfaced single weight paper with normal (2) and medium hard (3) emulsions were found quite satisfactory. These were developed in Defender 55-D, a cold tone developer and were mounted with Eastman dry mounting tissue.

All materials were fixed in Eastman prepared fixer.

The shadowless equipment pictures were taken with the Ernemann and one 100 watt lamp. The lamp was moved during a long exposure to eliminate all shadows. Exposure time was about one minute at $f/45.0$.

When powder pattern pictures were being taken the illumination was supplied by one 100 watt lamp placed 10 cm. from the magnet. Exposures with the Foth Derby were of the order of 5-10 seconds at 30X and 35-45 seconds at 80X.

Use was made of an RCA EMC-2 electron microscope to determine colloidal particle sizes. This instrument has a normal magnification of 5,000X. The magnification was increased to 15,000X by optical means. Exposures were made by reducing the intensity to a point where the image was just visible and then exposing Eastman Contrast Anti-abrasion plates for two seconds. The plates used were developed in DK60a at ninety degrees Fahrenheit. No apparent defects resulted from this harsh treatment.

Chapter IV

Particle Size Determination

Elmore[1] makes the statement that the particles which form the best patterns are those in the upper colloidal sizes. This would mean particles of the order of 10^{-5} cm. In order to determine the sizes of particles produced in this investigation use was made of both optical and electron microscopes. The procedure with the optical instrument **was** to compare the particles with precision ruled 1/10th and 1/100th millimeter scales (Figs. 27 and 28). When the electron microscope was used, comparison was made with the Dow 5800, lot 3584 latex spheres (Fig. 33). If the specimen to be examined was a true colloid or near colloid the electronic instrument was used. For larger particles the light microscope was found to be satisfactory.

The 1/10 mm. scale was also used as a means of measuring the observed patterns. The length indications on the pattern photographs were obtained by referring to Figs. 29 and 30 as standards. These were taken at the same microscope powers as the pattern pictures and were processed and enlarged in a similar manner.

Figs. 31 and 32 show two pattern-forming specimens. These are both hand-ground samples and indicate the smallest usable particles obtainable with this method. Comparison with the 1/100 mm. scale shows that the particles are of the order of 10^{-4} cm. or one micron. When magnified 100X there is no perceptible difference between patterns formed with these par-

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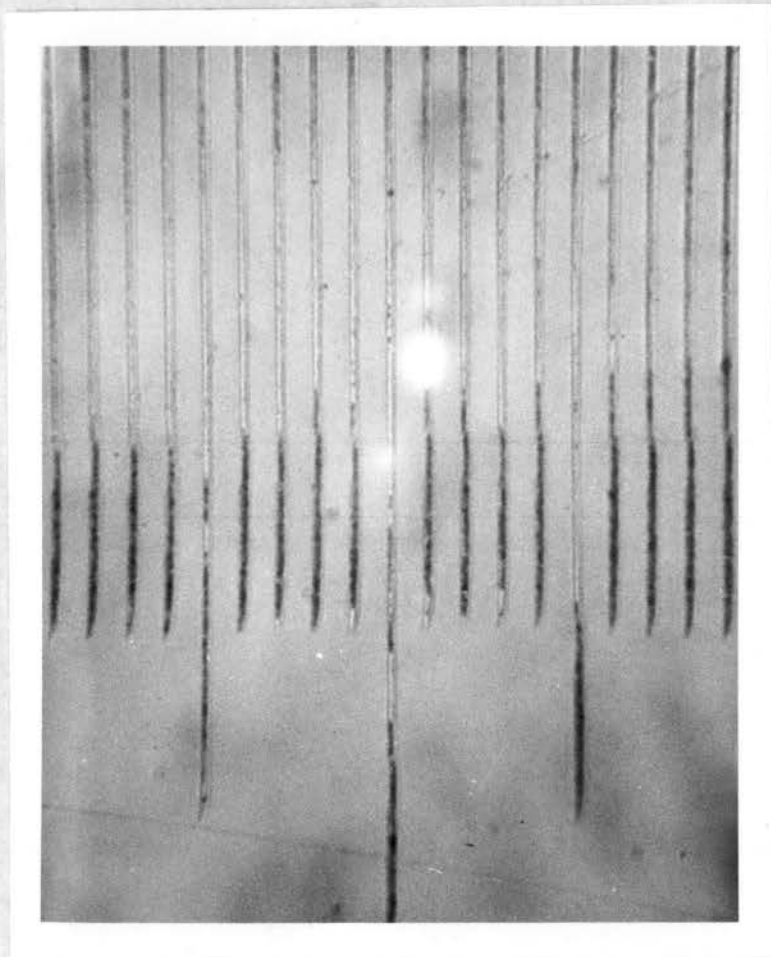[1] W. C. Elmore, Phys. Rev., Vol. 54, p. 309, 1938.

Fig. 27. 1/100 mm. scale used to determine
particle size (500X).

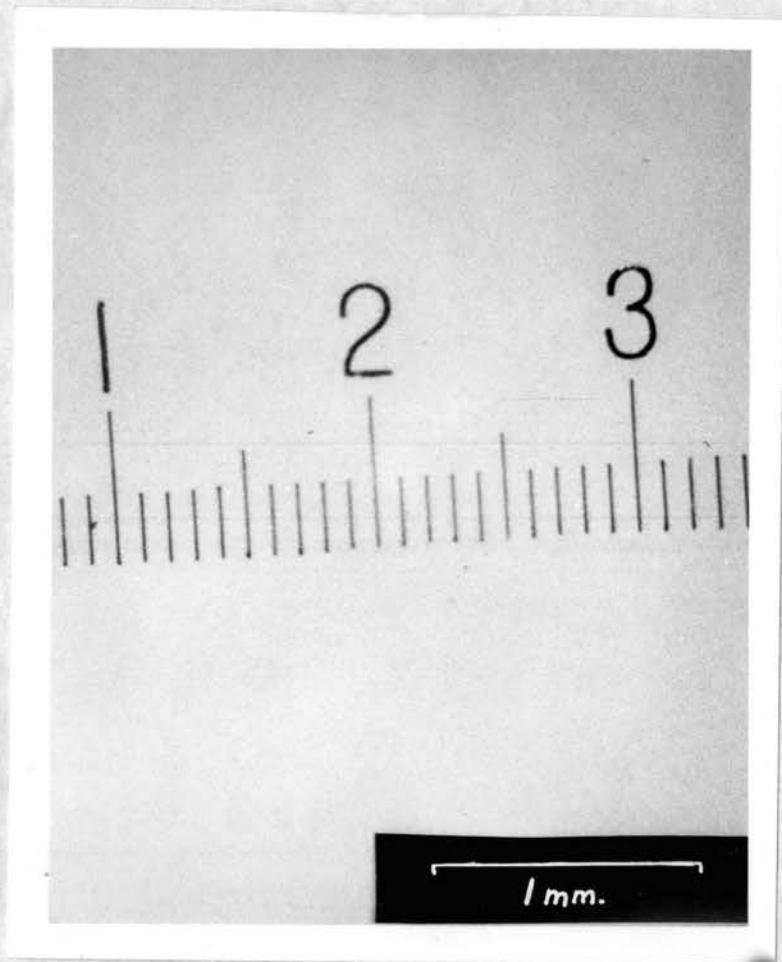Fig. 28. 1/10 mm. scale used to determine
particle size (500X).

E

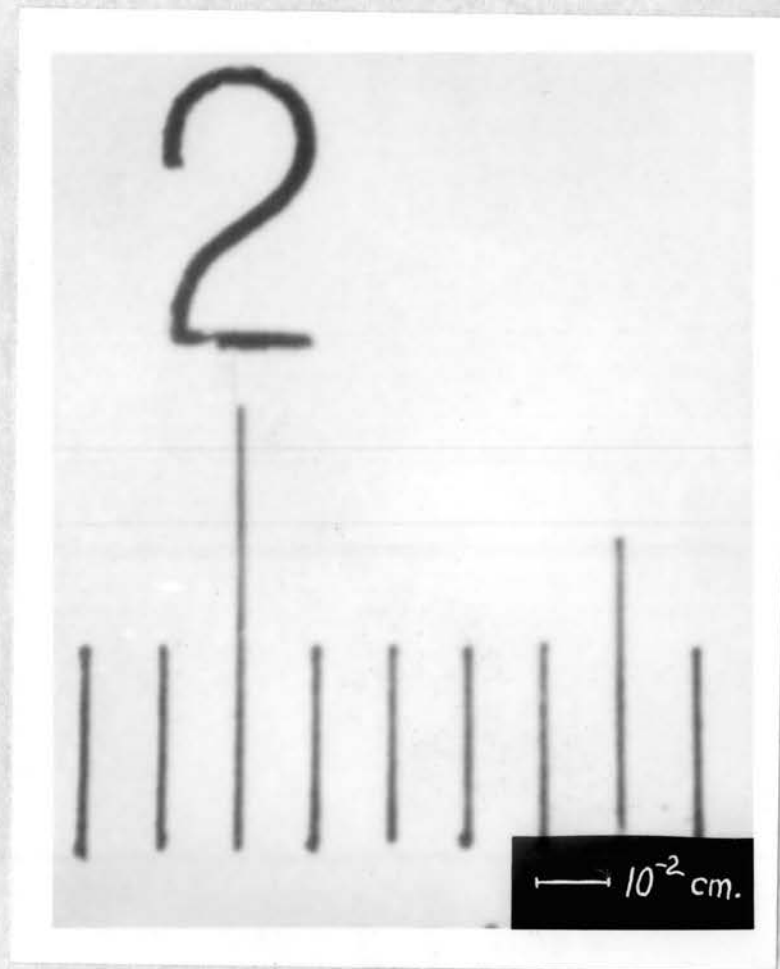Fig. 29. 1/10 mm. scale used to measure
patterns (35X).

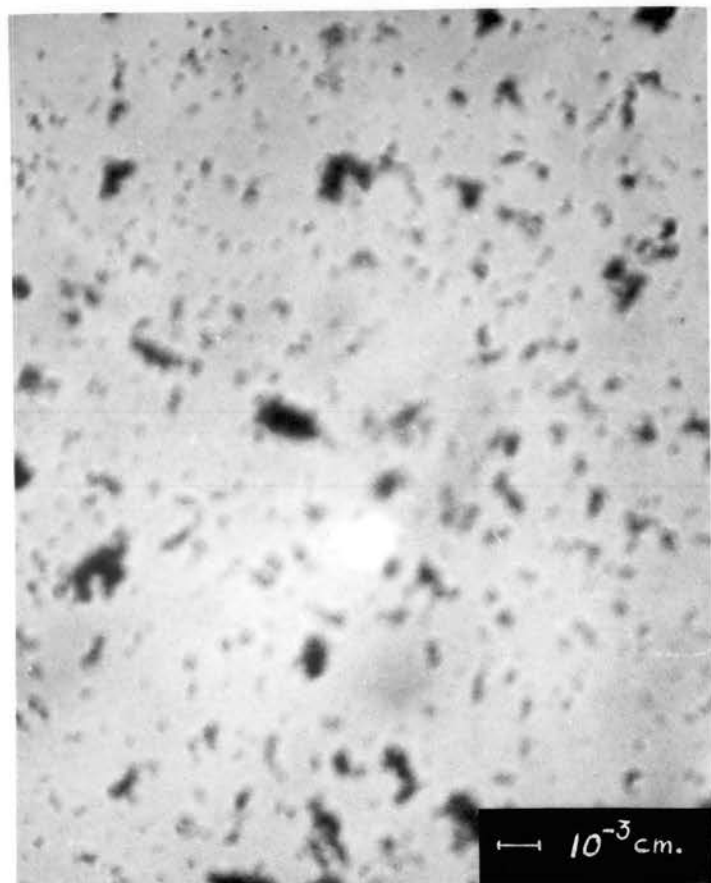Fig. 30. 1/10 mm. scale used to measure
patterns (100X).

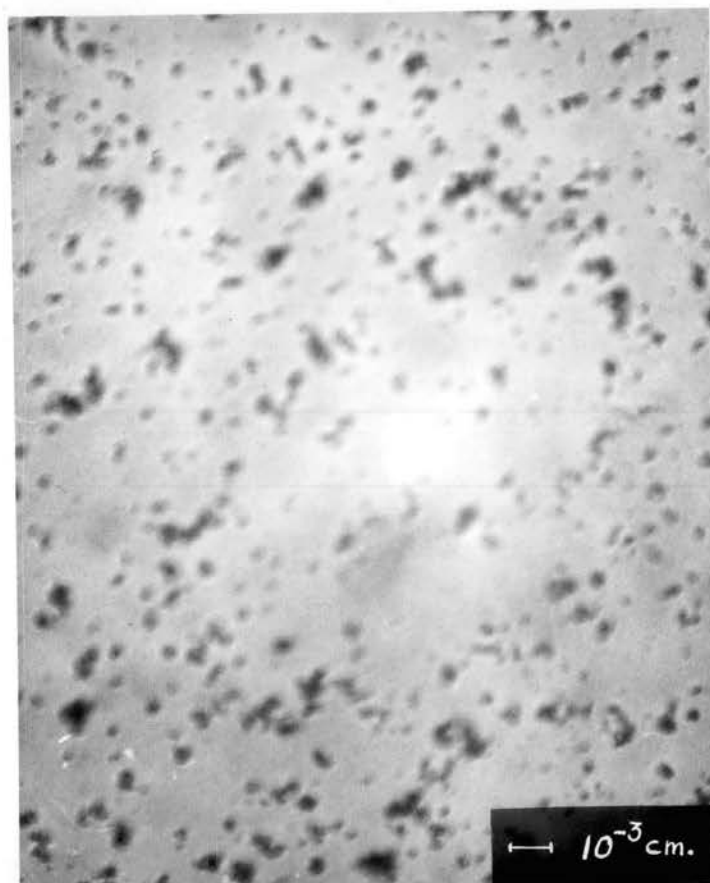Fig. 31. Magnetite (Fe_3O_4) ground from
colloid failure (500X).

Fig. 32. Ferric Oxide (Fe_2O_3) precipitated
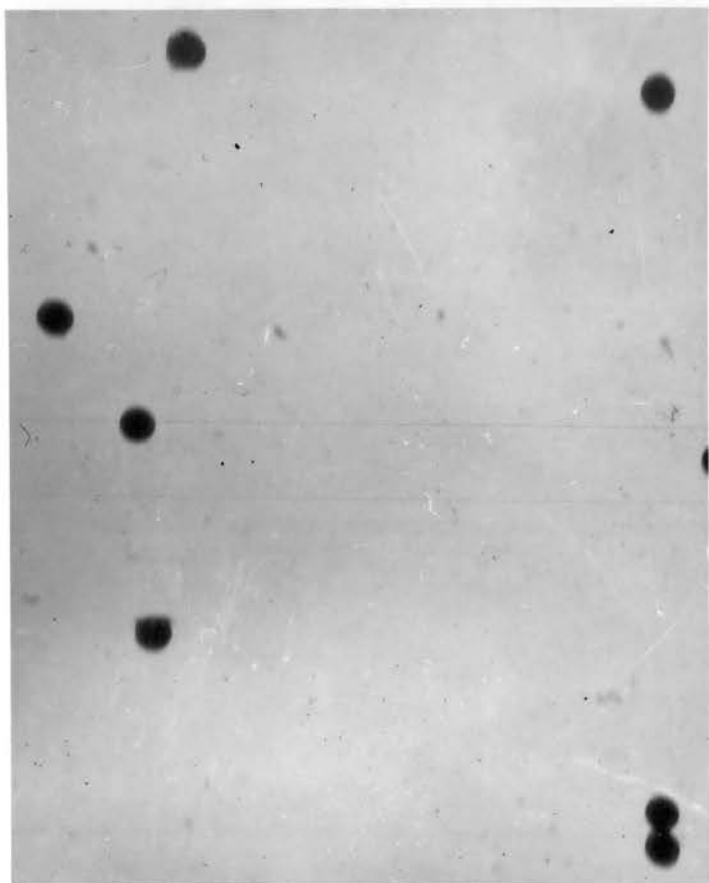from colloid formed while grinding (500X).

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Fig. 33. Dow latex 580G, lot 3584 used to
determine particle size. Diameter of
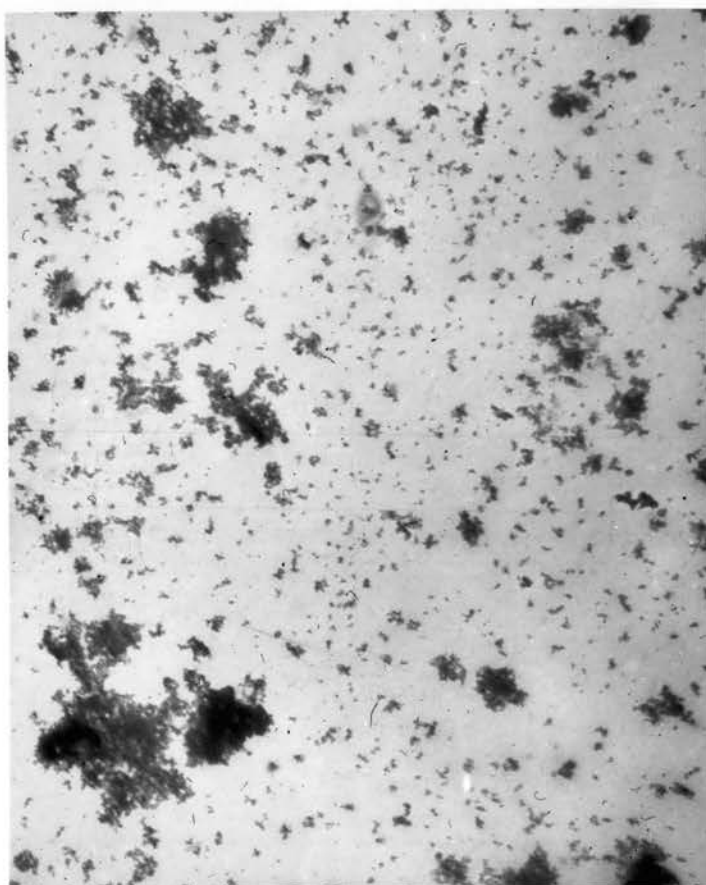spheres is $2.59 \cdot 10^{-5}$ cm. (15,000X).

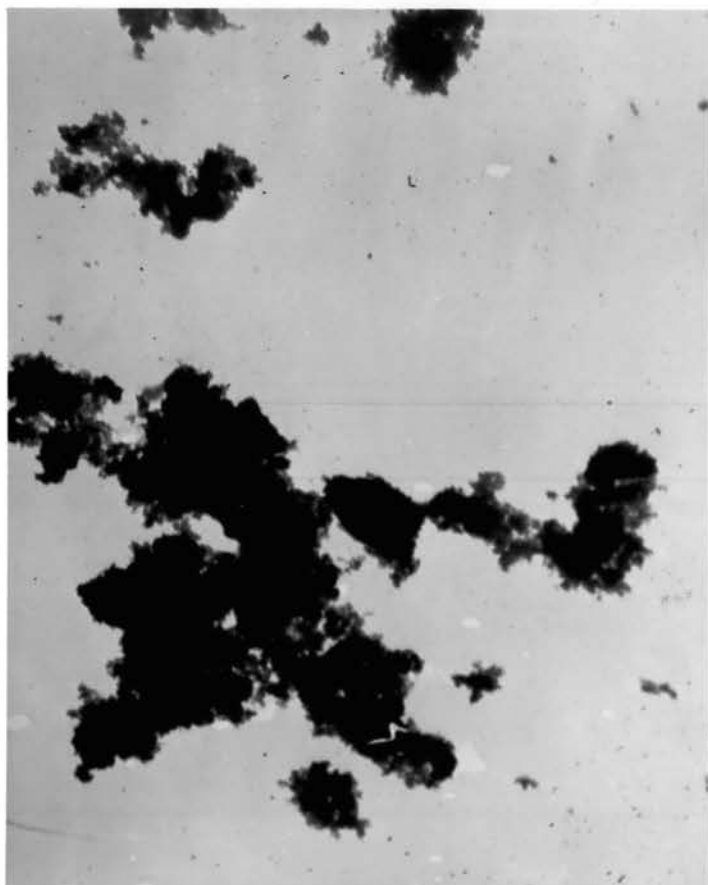Fig. 34. Particles precipitated from
colloid by boiling (15,000X).

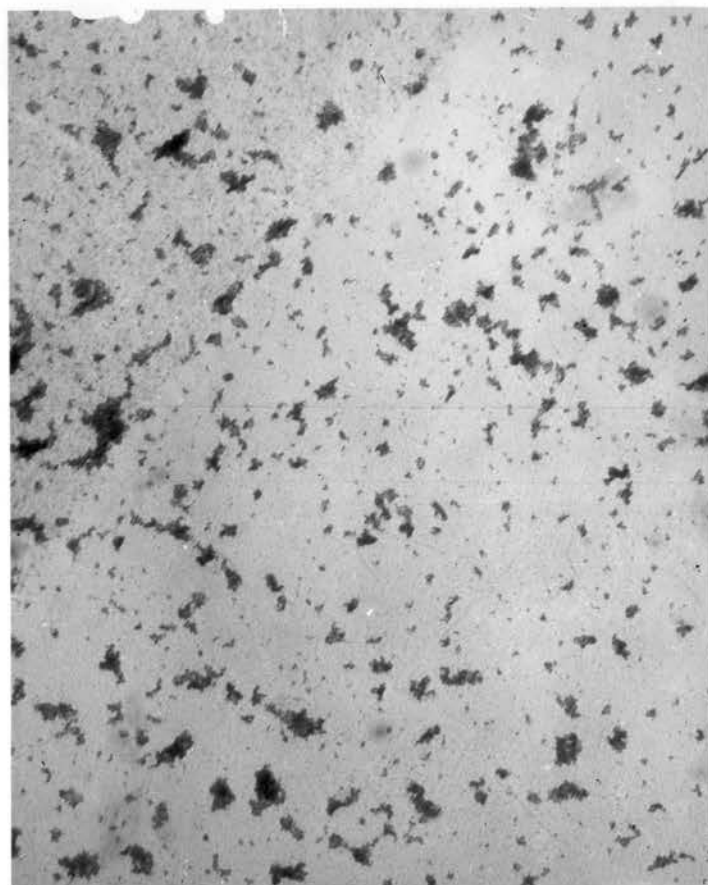Fig. 35. Prussian blue $(Fe_4(Fe(CN)_6)_3)$ precipitated from colloid (15,000X).

Fig. 36. Prussian blue $(Fe_4(Fe(CN)_6)_3)$ colloidal particles (15,000X).
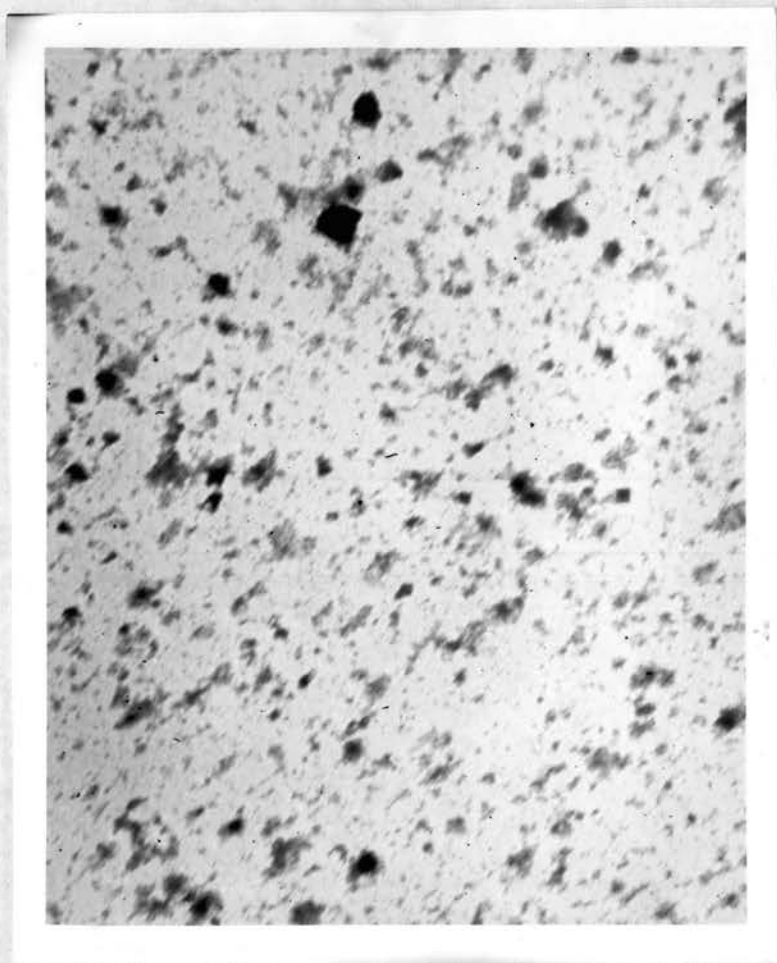
49

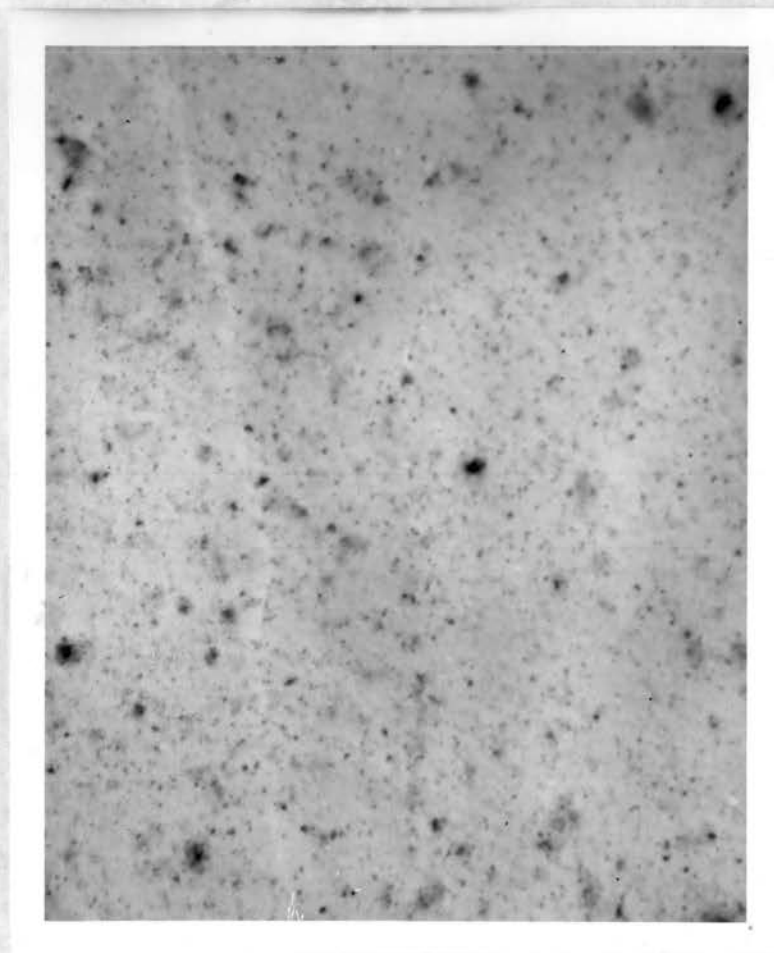Fig. 37. Pattern-forming Bozorth colloid (Fe_3O_4) (15,000X).

Fig. 38. True sol resulting from grinding of colloid failure. Particles are too small to form pattern (15,000X).

ticles and those formed by true colloids. Compare Figs. 25 and 6.

Particles precipitated from a colloid by boiling are shown in Fig. 34. When compared with the latex spheres we see that they are of the order of 10^{-6} cm. These particles are apparently Fe_2O_3 for they are brown and have been formed by exposing Fe_3O_4 to the atmosphere. The colloid resulted from grinding an Elmore colloid failure. Fig. 10 shows the fine pattern obtainable with these particles which are almost colloidal.

Ferric ferrocyanide formed patterns when the particles were large. When an Elmore failure was ground in kerosene particles of all sizes, including colloidal, were obtained. Figs. 35 and 36 show which particles precipitate after an interval and which remain colloidal in that order. Neither of these specimens produced acceptable patterns. The larger particles formed visible structures which corresponded to known patterns but the entire effect was nebulous. The small particles showed no pattern whatsoever. Apparently the magnetic attraction for these relatively large particles is too weak to cause their precipitation onto the magnet's surface.

Fig. 37 illustrates the proper particle size for a macroscopically magnetic specimen (Fe_3O_4). These are of the order of 10^{-6} cm. Particles smaller than these which do not form a pattern are shown in Fig. 38. These are smaller than 10^{-6} cm.

Chapter V

Results and Suggestions

The problem associated with this investigation was the production of particles which would show patterns indicative of the structure of ferromagnetic materials. A general result is that all the compounds of the ferromagnetic elements used (see list p. 49) were capable of forming patterns if the particles were of the proper size. This size is in agreement with the work of Elmore (see p. 40) for particles of the order of 10^{-4} to 10^{-6} formed the best patterns. Dimensions of this order of magnitude place the particles in the almost colloidal and just colloidal ranges. Larger particles obliterate the fine structure of the patterns while smaller ones do not precipitate out until the medium has evaporated.

Hand grinding of commercially available compounds yields particles the smallest of which are about one micron. This method does not have a very good yield for some substances and for others does not work at all.

The chemical production of colloidal Fe_3O_4 (Elmore type) was the best method of obtaining a fine pattern. Even though a water medium is used there is no staining of the magnet as the protecting soap prevents the water from acting on it. This method gave such good results that it was tried on other compounds none of which became colloidal of the proper particle size. Grinding such failures in kerosene leads to particles much smaller than available by grinding commercially prepared chemicals.

For demonstration purposes the hand grinding method is recommended. Rust ground in kerosene yields particles almost in the colloid range and

Substances Which Formed Patterns

Iron

Ferrous carbonate

Ferrous ferrocyanide

Ferric ferrocyanide

Ferrous oxide

Ferrosoferric oxide

Ferric oxide

Ferrous orthophosphate

Ferric orthophosphate

Ferric pyrophosphate

Ferrous sulfide

Nickel

Nickel compounds corresponding
  to those of iron

Cobalt compounds corresponding
  to those of iron

Cobalt sulfite

these form very delicate patterns. The patterns form immediately upon application of the mixture to the polished magnetic surface and the color of the rust gives a good contrast for photographic purposes without special lighting equipment.

It is believed that better photographic results would have been obtained if a ground glass focusing camera with four inch lens had been available. Such a camera together with a microscope capable of forming a flat field would eliminate the difficulties experienced with grain, nonuniformity of field and bulkiness.

While this article was in the process of being written other interesting possibilities of particle formation were discovered. Mention is made of a low voltage, high current arc[1] capable of producing colloids. Perhaps this method would not cause the breaking down of the medium experienced with the high voltage equipment. Mechanical grinding mills[2] as used in industry for paint and ceramic production are also a potential source of pattern-forming particles. J. C. Slater[3] describes the use of magnetic recording tape for powder pattern purposes and Kittel, Galt and Campbell[4] give a different chemical method of colloid production wherein particles are formed in the mixture by reduction. Added to these is the production of powdered iron slugs used in radio frequency work. This and other concepts of powder metallurgy might be found fruitful.

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[1] J. C. Ware, The Chemistry of the Colloidal State, p. 191.

[2] P. M. Travis, Mechanochemistry and the Colloid Mill.

[3] J. C. Slater, Physics Today, p. 12, January 1949.

[4] C. Kittel, J. K. Galt and W. E. Campbell, Phys. Rev., Vol. 77, p. 725, 1950.

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