NRL REPORT R-3491

COPY NO. [redacted]

FR-3491

THE PRODUCTION OF METALLIC FLAKES FOR ABSORBING MICROWAVES

NAVAL RESEARCH LABORATORY

WASHINGTON, D.C.

[redacted] UNCLASSIFIED

NRL REPORT R-3491

COPY NO. 48

UNCLASSIFIED

THE PRODUCTION OF METALLIC FLAKES FOR ABSORBING MICROWAVES

DECLASSIFIED

George Sandoz

June 29, 1949

UNCLASSIFIED By Authority of NRL Classification Change Notice No. 10-61 Dated 2 May 1961
Doris A. Layfard
Entered by
2028
Code
UNCLASSIFIED

Approved by:

Dr. H. E. Stauss, Head, Electric Magnetic Alloys Branch
Dr. O. T. Marzke, Superintendent, Metallurgy Division

NAVAL RESEARCH LABORATORY
CAPTAIN F. R. FURTH, USN, DIRECTOR
WASHINGTON, D.C.

DECLASSIFIED

[redacted]

DISTRIBUTION

	Copy No.
BuShips	1
BuAer	2
BuOrd	3
CNO	4
CDR., Boston Naval Shipyard	5
CDR., Puget Sound Naval Shipyard	6
CDR., New York Naval Shipyard	7
CDR., Charleston Naval Shipyard	8
CDR., Pearl Harbor Naval Shipyard	9
CDR., Philadelphia Naval Shipyard	10
CDR., Portsmouth Naval Shipyard	11
CDR., Norfolk Naval Shipyard	12
CDR., San Francisco Naval Shipyard	13
CDR., Terminal Island Naval Shipyard	14
CDR., Mare Island Naval Shipyard	15
CDR., USNGF	16
CO, USNTS, Newport	17
Dir., USNEL	18-19
CDR., USNOTS Attn: Reports Unit	20-21
OCSigO Attn: Ch. Eng. & Tech. Div., SIGTM-S	22

CONTENTS

ABSTRACT

An investigation was undertaken in order to provide a supply of metallic flakes made under controlled conditions for use in absorbent material for radio waves. Studies were made of size, shape, and structure of metal powders and of flakes as related to their absorptive properties.

The results indicate that flake quality for use in absorbent materials is mostly dependent on the properties of the metal powders flaked. Impure carbonyl iron (grades E, TH, and SF) produced the best absorbing material, apparently because of small grain size or magnetic softness.

PROBLEM STATUS

This is an interim report on one phase of the problem; work is continuing.

AUTHORIZATION

NRL Problem No. R11-14R

THE PRODUCTION OF METALLIC FLAKES FOR ABSORBING MICROWAVES

INTRODUCTION

In November 1945, the Metallurgy Division undertook the production of metallic flakes for use in absorbent materials for radio waves to ensure a supply made under controlled conditions. The requirements called for flakes with thicknesses between 0.25 and 5 microns and with ratios of diameter to thickness of 20 to 100, to be produced from commercial powders of magnetic metals. Production began in September, 1946.

It soon became evident that differences in absorbent material obtainable through control of flake diameter and thickness were less important than differences resulting from other properties of the powders. Consequently, after the preliminary investigation of the quality of the flaked metal as a function of the flaking technique, emphasis was diverted to a search for clues to those physical properties in powders which led to desirable flakes.

PRODUCTION OF FLAKES

The principle of the flaking process used is described in the Everett Joel Hall patents No. 1569484 and No. 2002891. The choice of equipment was based on the recommendations of Metals Disintegrating Company, Elizabeth, New Jersey, which generously supplied drawings and specifications of machines, information as to their use in flaking operations, and general advice on the production of metallic flakes.

The flow sheet of the production of flakes is as follows:

MILLING
↓
FILTER PRESS
↓
VACUUM DRYING
↓
SIFTING → REJECT
↓
STORAGE
↓
TEST

The milling is done in a ball mill with a 36 inch drum of cast SAE 4340 steel, designed to maintain a neutral atmosphere. Variable operating speeds are secured with a Reeves No. 0 Varispeed transmission and a 3-hp induction motor. A charge of 128 lbs (45%) of 5/16 inch diameter and 157 lbs (55%) of 1/4 inch steel balls; 4,000 to 7,000 cc of mineral spirits; and 0.4 lbs of stearic acid are used with each batch of powder. After milling, the mineral spirits are removed with a pressure filter press operating at 25 lbs/in. from a tank of CO_2 and using an 18-oz twill filter cloth. The filtered fluid is returned to the ball mill to remove the remaining flakes.

The cake from the filter is dried in a Divine Vacuum Dryer No. 0 with internally heated shelves. The vacuum is secured with a Kinney VSD 556 vacuum pump. A water-cooled condenser between the vacuum pump and dryer collects the distilled vapors of mineral spirits. In order to prevent oxidation and burning of the filter cake, it is necessary to develop the best obtainable vacuum (23 mm Hg) in the drying chamber before steam is admitted to the shelves, and at the end to cool the cake in the vacuum. The vacuum is released by admitting CO_2 into the chamber. Since the metal flakes always show a tendency to heat and burn spontaneously, it is necessary to keep them in a neutral atmosphere or under a cover of dry ice. After drying, the sintered lumps of flakes are broken in a dust-tight sifter with brushes on spiders rotating at 120 rpm. and sifted through a 100-mesh screen. To eliminate the hazard of an explosion, a stream of CO_2 gas is admitted through the lid of the sifter to envelop the powder.

EXAMINATION OF FLAKES

The absorbent properties of the flakes, usually compounded in rubber, are measured by the Radio Division I. Tests of other chemical properties of the flakes, flake structure, and flake magnetic properties are conducted in the Metallurgy Division in an effort to correlate them with absorbent properties, neglecting the influence of the compounding operation.

Chemical Properties

A list of the powders flaked and of their compositions, particle sizes, and apparent densities is given in Table 1.

Flake Structure

Because theoretical studies indicate that for a given alloy the ratio of average flake diameter to thickness is a measure of the value of the flakes in absorbing materials, both diameter and thickness were measured. The methods used, adapted from two known techniques, are described briefly in the Appendix. In addition, flakes were molded in Lucite, and cross sections obtained by making use of the circumstance that the grains of Lucite were larger than the flakes and the latter became aligned in the grain boundaries. By this method it was found possible to estimate flake thickness, and several measurements gave values roughly comparable to those from other methods used. Such determinations from Lucite specimens, however, are not included in the data.

In Table 2 is given a list of flake batches with the milling techniques used, flake diameters, thicknesses, ratios of diameter to thickness, and apparent densities. Figure 1 shows the variation of flake thickness, diameter, and diameter-thickness ratio with milling time for electrolytic iron flakes milled under identical conditions; Figure 2 shows similar curves for Sendust flakes. It can be seen that flake thickness decreases rapidly at the beginning of milling, and, for Sendust, appears to approach a constant minimum value. This

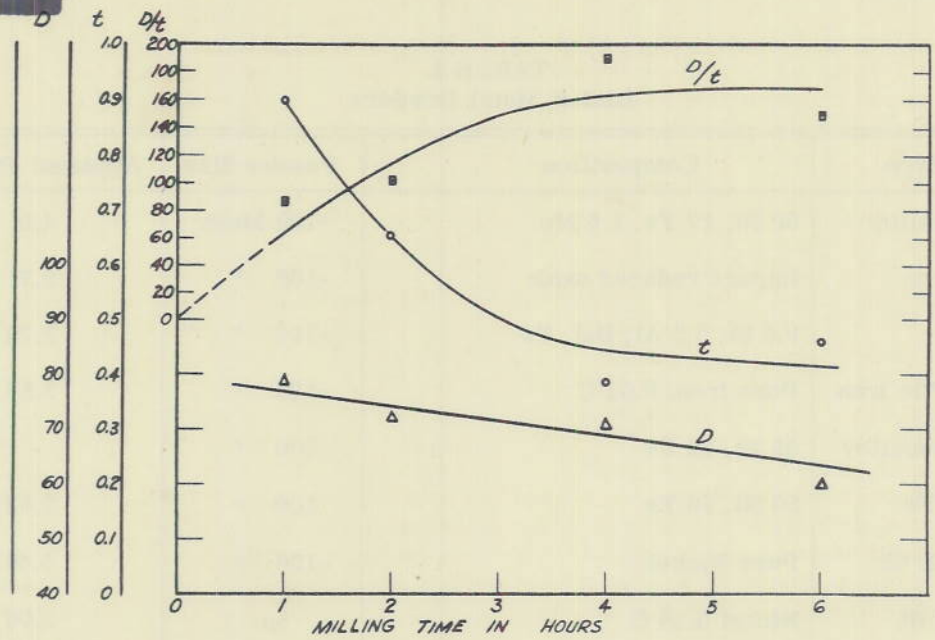


Fig. 1 - Effect of milling time upon the diameter, thickness and diameter to thickness ratio for electrolytic iron powder

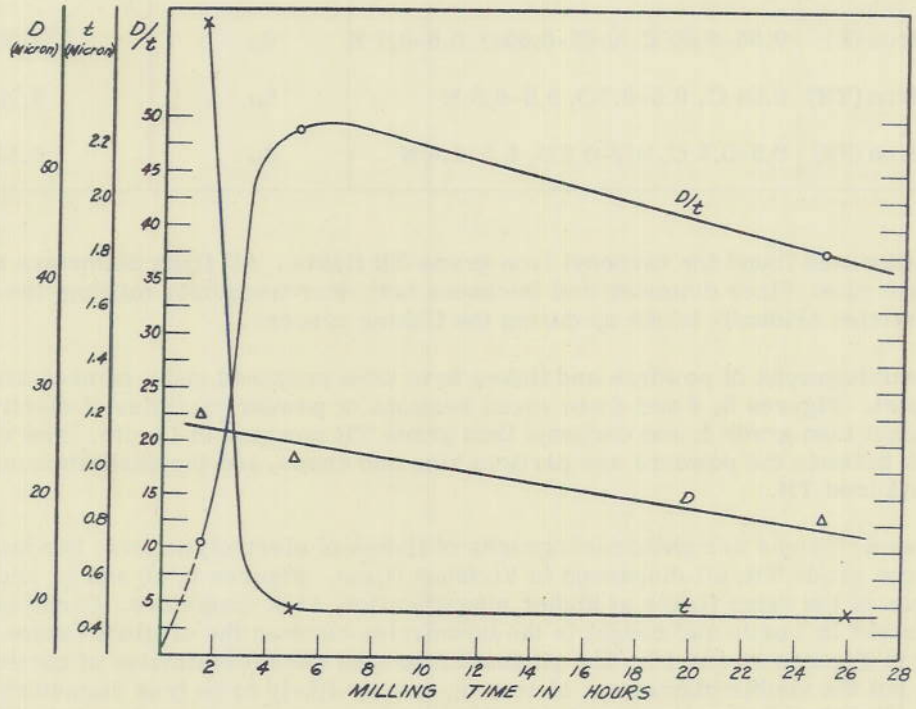


Fig. 2 - Effect of milling time upon the diameter, thickness and diameter to thickness ratio for Sendust powder

TABLE 1
List of Metal Powders

Powder Type	Composition	Powder Size	Apparent Density
Mo Permalloy	80 Ni, 17 Fe, 1.6 Mo	-100 Mesh	4.0
Sponge Iron	Impure reduced oxide	-100 "	2.71
Sendust	9.5 Si, 5.5 Al, Bal. Fe	-100 "	3.72
Electrolytic Iron	Pure Iron, 0.01 C	-100 "	2.58
45 Ni Permalloy	45 Ni, 55 Fe	100 "	-
50 Ni 50 Fe	50 Ni, 50 Fe	100 "	2.63
Nickel MD 85	Pure Nickel	-100 "	4.46
Carbonyl Ni	Nickel 0.24 C	5μ	2.06
Carbonyl Iron (L)	Pure Iron	20μ	2.82
Carbonyl Iron (C)	Pure Iron	10μ	3.03
Carbonyl Iron (HP)	Pure Iron	10μ	3.16
Carbonyl Iron (E)	0.65-0.80 C, 0.45-0.60 O, 0.6-0.7 N	8μ	3.02
Carbonyl Iron (TH)	0.58 C, 0.5-0.7O, 0.5-0.6 N	5μ	3.20
Carbonyl Iron (SF)	0.5-0.6 C, 0.7-0.8 O, 0.5-0.6 N	3μ	2.51

same behavior was found for carbonyl iron grade TH flakes. All flake diameters decreased at a constant rate. Since diameter and thickness both decreased upon milling, the original powder particles evidently broke up during the flaking process.

Photomicrographs of powders and flakes have been prepared and a number are included in this report. Figures 3, 4 and 5 are cross sections of powder particles of electrolytic iron, carbonyl iron grade L and carbonyl iron grade TH mounted in Lucite. The visible differences between the powders are particle size and shape, and the shell structure of the carbonyl iron TH.

Figures 6, 7 and 8 are photomicrographs of flakes of electrolytic iron, Sendust, and carbonyl iron grade TH, all dispersed in Vistanex films. Figures 9, 10 and 11 are photomicrographs of the same flakes at higher magnification, 1500 diameters. Cross sections of flakes mixed in Lucite and caught in the boundaries between the original Lucite particles are shown in Figures 12 and 13. The photomicrographs permit estimates of particle thickness, but the visible diameters, of course, are not likely to be true diameters. Flake diameters of carbonyl iron as observed in Figure 13 are clearly much less than the diameters seen in Figure 11 in Vistanex films. The flakes as seen in Vistanex films seem

TABLE 2
Characteristics of Flakes by Batches

No. Material	Weight of Batch (lb)	Milling Time (Hr)	Mill Atmos-phere	Ball Size & Distribution	Flake Thickness (μ)	Flake Diameter (μ)	D/t	Apparent Density (g/cc.)
1. Mo Permalloy	5	7	air	128 lb. 5/16" D. 157 lb. 1/4" D.	0.33	10.1	30.4	0.546
2. Electrolytic Iron	3	1	He	" "	0.90	79.2	88.0	0.209
3. " "	3	2	"	" "	0.66	73.7	101.0	0.226
4. " "	3	4	"	" "	0.385	71.8	188.0	0.237
5. " "	3	6	"	" "	0.46	60.4	135.0	0.304
6. Carbonyl Iron TH	4	3	"	" "	0.825	18.5	22.4	1.47
7. " " "	5	6	"	" "	0.55	14.5	26.4	1.00
8. Carbonyl Nickel	5	3	"	" "	0.238	21.0	88.4	0.433
9. Nickel MD 85	3.5	3	"	" "	0.435	43.2	99.1	0.389
10. Carbonyl Iron TH	16	11.5	"	" "	0.466	16.9	36.2	1.10
11. 50 Ni 50 Fe	4	4	"	" "	0.270	24.2	89.6	0.414
12. Sendust	4	5	CO_2	" "	0.480	23.9	49.3	0.360
13. Sponge Iron	4	4	"	" "	0.265	32.8	124.0	0.282
14. Sendust	5	25	"	108 lb. 5/16" D. 172 lb. 1/4" D.	0.485	18.5	37.9	0.43
15. Sendust	5	1.5	"	" "	2.68	27.8	10.4	1.76
16. Carbonyl Iron TH	15.1	45	"	" "	0.337	14.9	44.2	1.02

Fig. 3 - Electrolytic iron powder section through Lucite mounting, nital etch 1500x

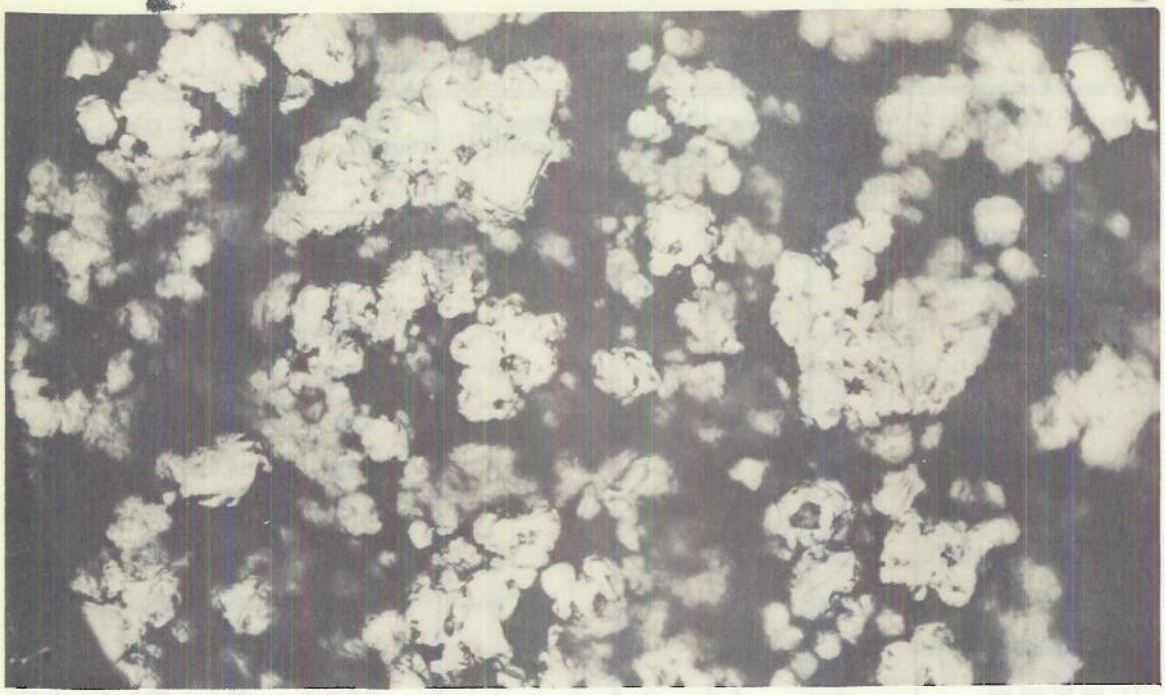


Fig. 4 - Carbonyl iron grade L section through Lucite mounting, nital etch 750x

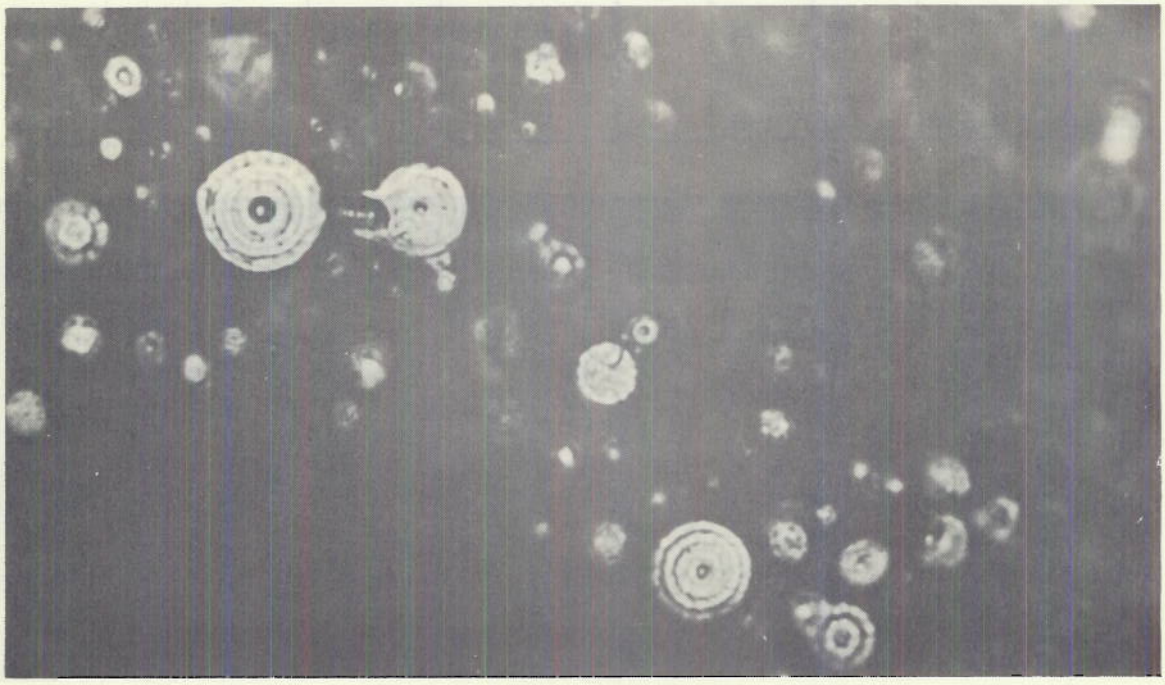


Fig. 5 - Carbonyl iron grade TH section through Lucite mounting, nital etch 2000x

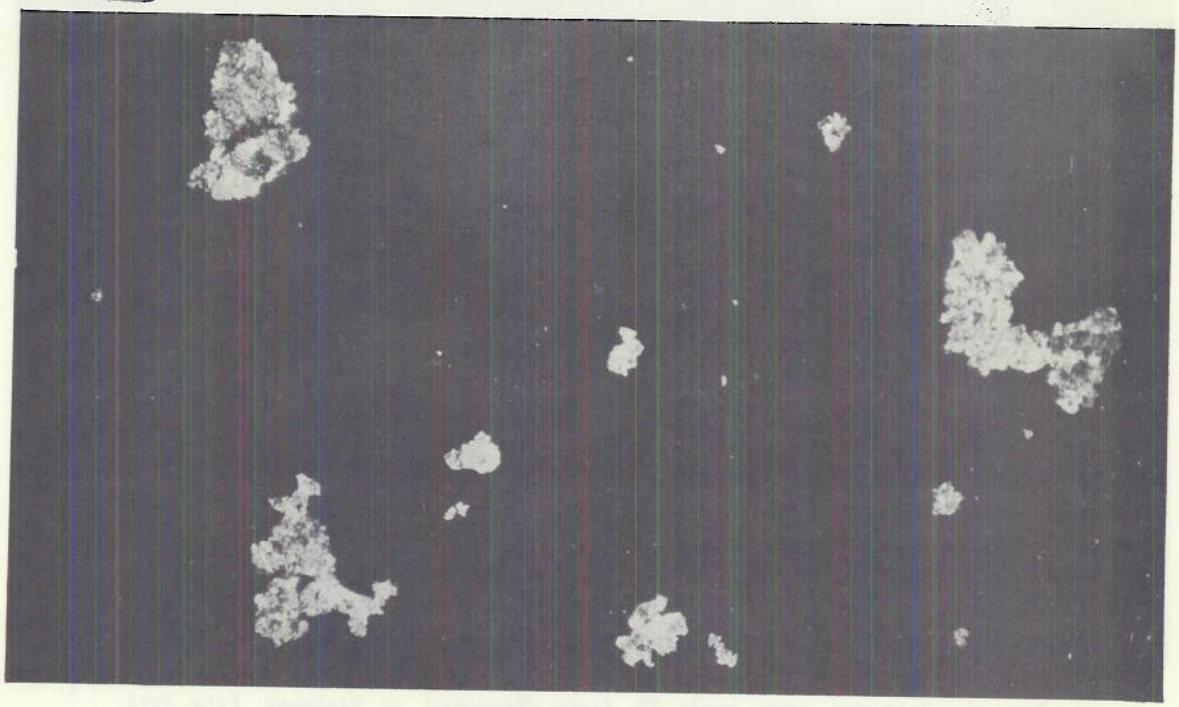


Fig. 6 - Electrolytic iron flake dispersed in Vistanex film, dark field, 75x

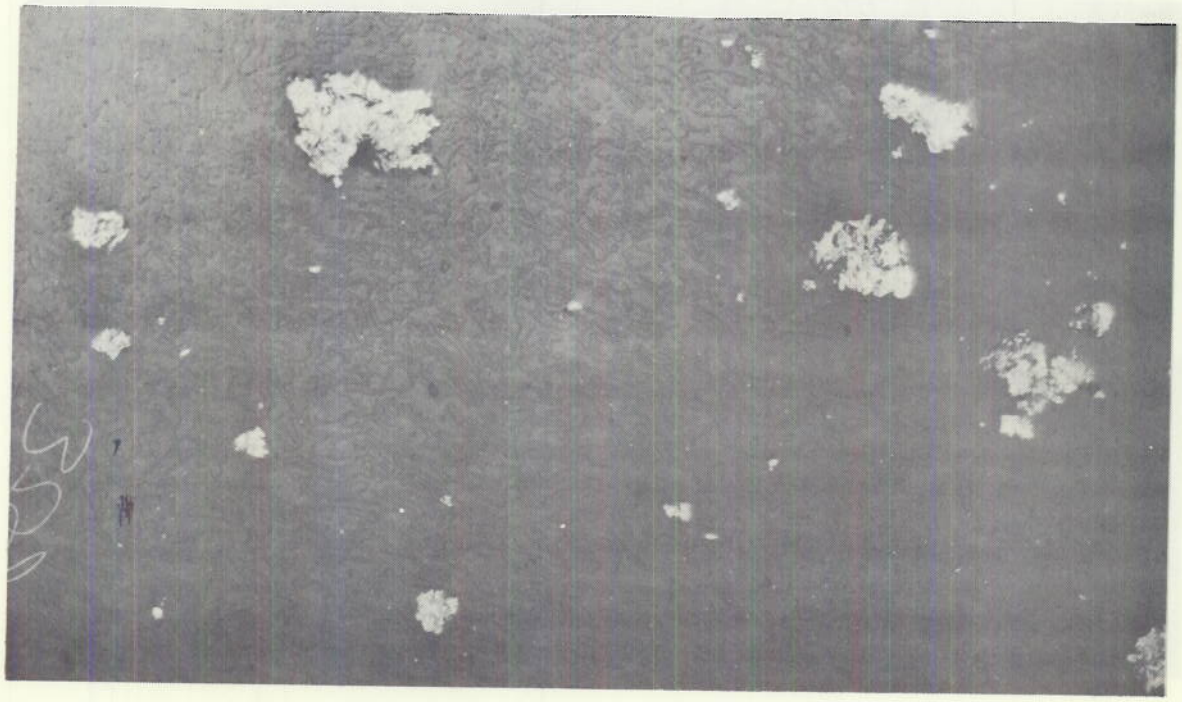


Fig. 7 - Sendust flake dispersed in Vistanex film, 300x

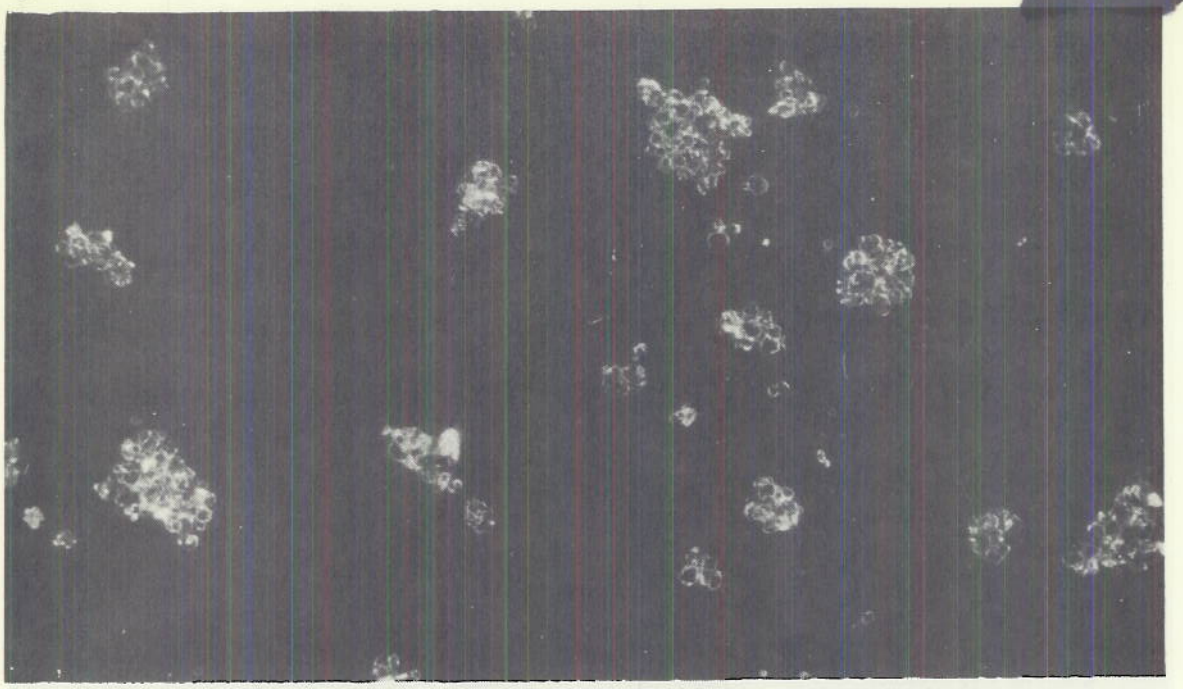


Fig. 8 - Carbonyl iron grade TH flake dispersed in Vistanex film, dark field, 300x

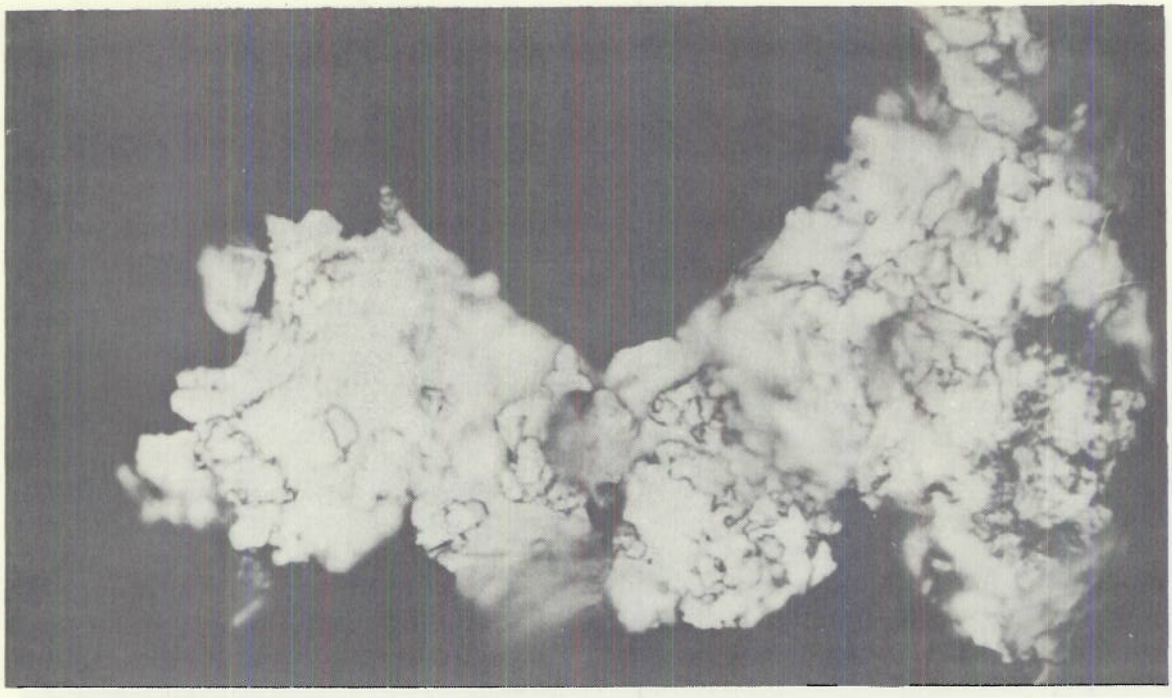


Fig. 9 - Electrolytic iron flake dispersed in Vistanex film, 1500x

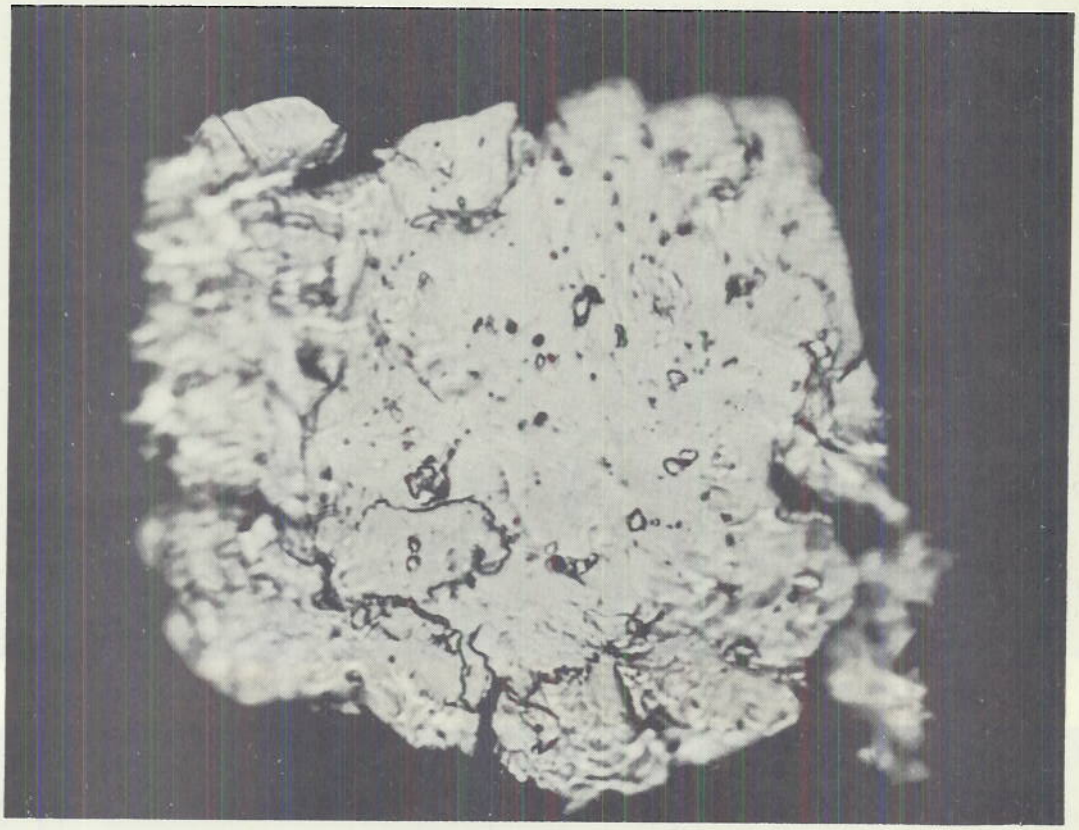


Fig. 10 - Sendust flake dispersed in Vistanex film, 1500x

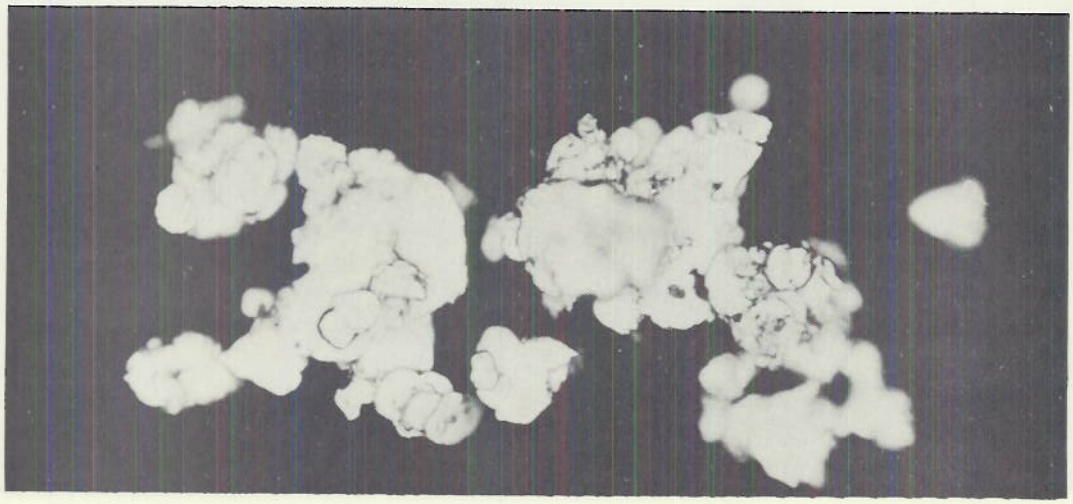


Fig. 11 - Carbonyl iron grade TH flake dispersed in Vistanex film, 1500x

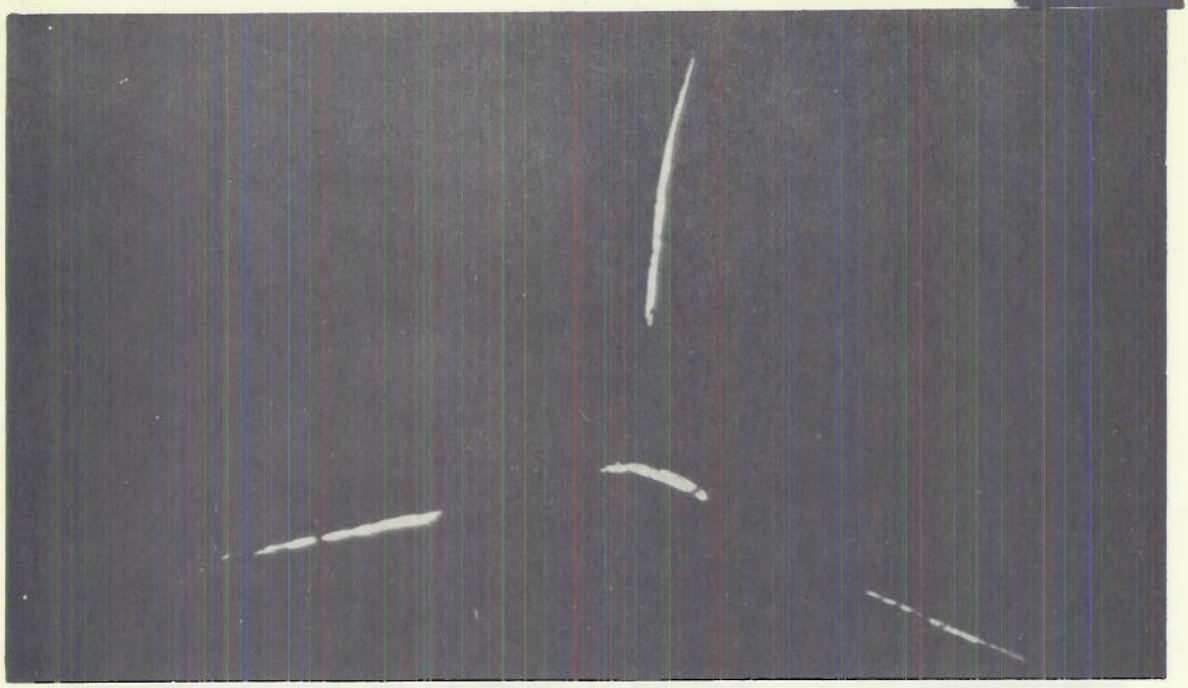


Fig. 12 - Electrolytic iron flake section through Lucite mounting, 1000x

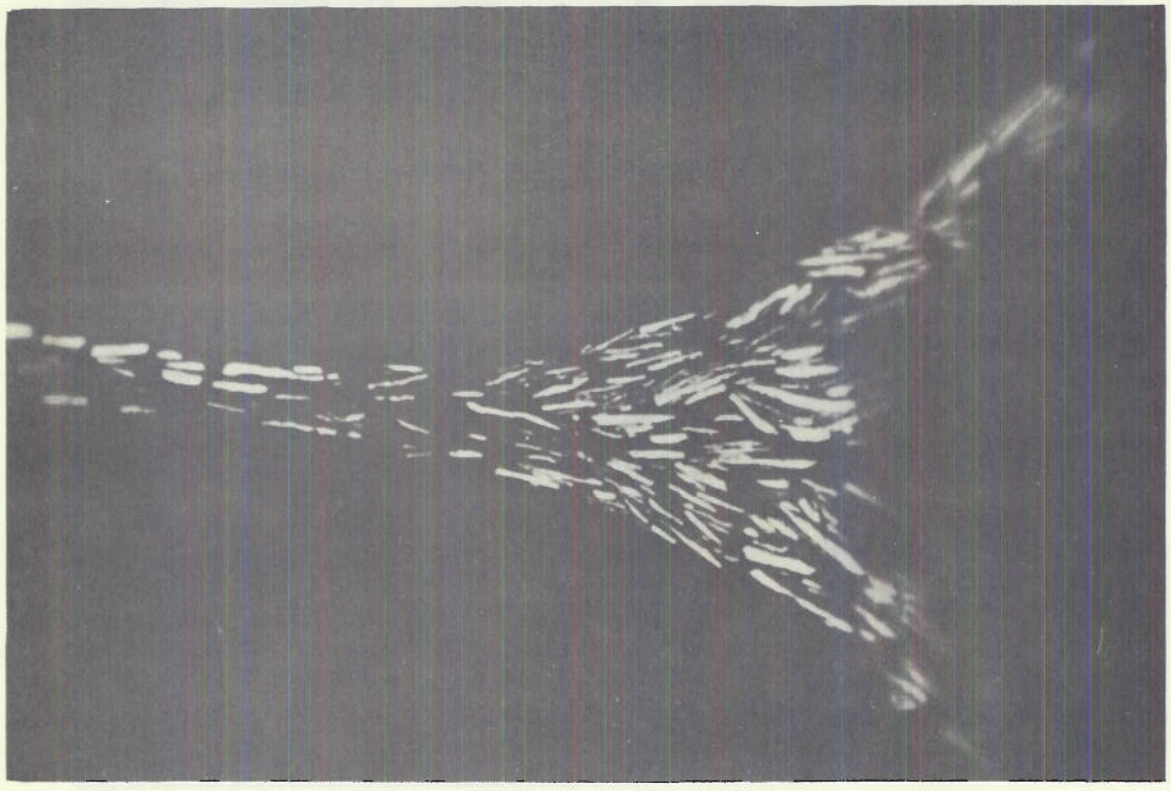


Fig. 13 - Carbonyl iron grade TH flake section through Lucite mounting, 1500x

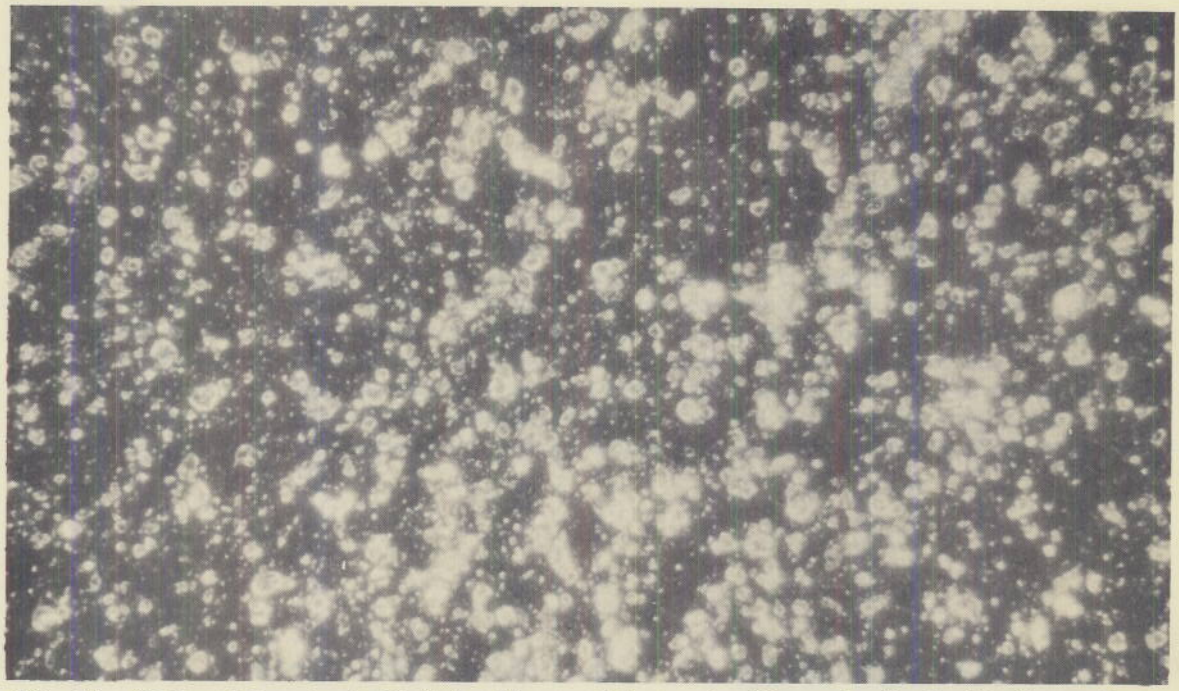


Fig. 14 - Carbonyl iron grade TH flake dispersed in acacia film and rubbed with finger, 300x

to be really aggregates of smaller components. Carbonyl iron TH flakes dispersed in acacia film were readily broken up into smaller particles by rubbing the film with the fingers, as shown by Figure 14. A similar phenomenon was observed upon rubbing the surface of Vistanex films.

A search made by the Optics Division with the electron microscope for structures in carbonyl iron not revealed by the metallograph was unsuccessful. Attempts to use electron diffraction on carbonyl iron powders E and TH failed to produce a diffraction pattern.

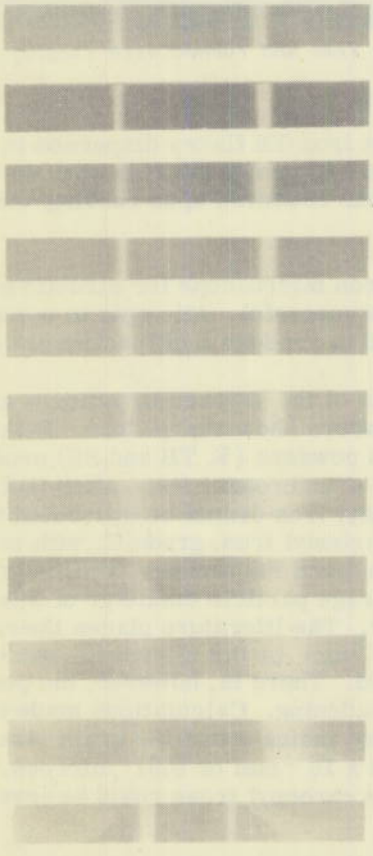
More success was had with X-ray diffraction. Prints of the diffraction patterns are given in Figure 15. Sponge iron and electrolytic iron powders show sharp lines. Flaking broadened the lines. The impure grades of carbonyl iron powders (E, TH and SF) produced broader lines than the other powders and flakes and gave even broader lines after flaking. The extremely broad lines of the impure grades of carbonyl iron cannot be attributed to fine particle size. A comparison of the line breadth of carbonyl iron, grade C, with carbonyl iron, grade E, reveals that the lines of grade E are much the broader, yet the grade E powder is reported by the manufacturer to have an average particle diameter of 8 microns as compared to 10 microns for the C grade powder. The literature places the critical size of particles for line broadening at about 2×10^{-4} mm or 0.2 microns,[1] which is smaller than the particle size of any of the powders tested. There is, however, the possibility that grains within the particles cause the line broadening. Calculations made with the Scherrer formula relating grain size to line broadening indicate that the grain size in the impure carbonyl irons should be of the order of 1.3×10^{-5} mm or 0.01 microns.[1] Another possible reason for the broad lines of the impure carbonyl irons could be crystal

[1] Sproull, W. T., "X-rays in Practice," p. 446, McGraw-Hill, 1946

imperfection such as strains caused by the presence of impurities. Carbon, oxygen, and nitrogen are present in these powders in larger amounts than in the powders producing sharp diffraction lines.

Magnetic Properties

Theoretical considerations had shown that soft magnetic characteristics were desirable in absorbers. A simple means was used to compare the residual magnetism in the various flakes. The flakes were packed tightly into small test tubes, and the filled tubes were magnetized by means of a strong permanent magnet and dipped into a jar of iron flakes. The residual magnetism was compared by the amount of flakes which adhered after the magnet was removed. Sendust alloy and the impure carbonyl iron, grades TH and SF, reported to be the materials that gave the best performance in the absorbent films, gave no indication of residual induction in either powder or flakes except after prolonged milling. The other materials all showed residual magnetism in the flake form and some in the powder. It would appear that magnetic softness is important in flakes for absorbers.



A. Sponge Iron Powder

B. Electrolytic Iron Powder

C. Electrolytic Iron Flake

D. Carbonyl Iron Grade L Powder

E. Carbonyl Iron Grade C Powder

F. Carbonyl Iron Grade C Flake

G. Carbonyl Iron Grade E Powder

H. Carbonyl Iron Grade TH Powder

I. Carbonyl Iron Grade TH Flake

J. Carbonyl Iron Grade SF Powder

K. Carbonyl Nickel Powder

Fig. 15 - X-ray diffraction pictures of powder and flake showing line broadening effects

CONCLUSIONS

1. For a given original powder, the flaking treatment (or the final size and shape of the flakes), within the limits of the present work, is of minor importance in the final absorber of radar waves; but the flakes are better than the original powder.

2. The performance of metal flakes in absorbers is closely dependent upon the original powder.

3. Flakes of Sendust and of the impure grades of carbonyl iron (E, TH, and SF) show the best performance in absorbers at radar frequencies.

4. The superiority of some powders in absorbers has not been related to other properties, but it is possible that the superiority may arise from small grain size or from magnetic softness.

* * *

APPENDIX
Measurement of Diameter-Thickness Ratio

To measure flake diameters microscopically, it is necessary to produce a uniform dispersion with the individual flakes lying flat on a glass slide. This is done by preparing Vistanex films in which the flake particles are dispersed.[2] The first step is to prepare a slurry of the flake in a solution of Vistanex in a naptha-xylene solvent. The composition found to be most satisfactory is:

Flake powder	0.7 g.
Vistanex (7.5% by weight in 50-50 naptha-xylene)	8.0 g.
Solvent (50-50 by volume) added to bring total weight of No. 38 naptha and xylene up to	50.0 g.

A drop of slurry is placed on the surface of a dish of clean water containing a wetting agent (Daxad No. 11) added to the amount of 0.0001% for proper spreading of the film. The drop spreads out rapidly and then shrinks back as the solvent evaporates, leaving a small film which is pickup up on a glass slide.

The average flake diameter is determined by photographing areas of the Vistanex film. Particles are measured to the nearest millimeter at their maximum width along the x-axis. The root-mean-square diameter is calculated by use of the formula

$$\overline{D} = \sqrt{\frac{\Sigma F_i \ D_i^2}{\Sigma F_i}}$$

where F_i = number of particles in size class i.
D_i = diameter of size class i, and the summations are taken over all the classes i.

The average thickness of the flake is measured on water in a tray such as is used to measure the covering power of paint pigments.[3] The assumption is made that the flake forms a uniform continuous film on the water surface, and the thickness is calculated from the surface area covered, the weight of the flake, and specific gravity of the metal.

---

[2] "Characterization of Metal Flakes—Determination of Diameter-Thickness Ratio," Chemical Department Experimental Station, E. I. Dupont De Nemours and Company ESP-45, 387.

[3] Edwards, J. D. and Mason, R. B., "Covering Capacity (on Water) of Aluminum Bronze Powder," Industrial and Engineering Chemistry, Analytical Edition, V. 6, p. 159, 1934.

The weighed flake is soaked in acetone on a small watch glass and the edge of the watch glass dipped slowly into the water. This causes the flake to spread out rapidly and evenly over the water, and helps prevent overlapping during subsequent compression of the film by the two glass slides used to manipulate the film on the tray. A stream of air bubbled through acetone and blown on top of the film is helpful in breaking up lumps of flake and producing a more uniform film.

* * *