KM-51-52 PARTICLE SIZE DISTRIBUTION OF PIGMENTARY BETA PHASE COPPER PHTHALOCYANINE By: A. R. Hanke 2/6/

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# NEWARK PLANT
# PIGMENT COLOR RESEARCH REPORT

Final Report

## PARTICLE SIZE DISTRIBUTION OF PIGMENTARY BETA PHASE COPPER PHTHALOCYANINE

Period Covered 2/6/51 to 4/9/51

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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

Final Report

# PARTICLE SIZE DISTRIBUTION OF PIGMENTARY BETA PHASE COPPER PHTHALOCYANINE

2/8/51 to 4/9/51

Charge: 1101-11-20



SUBMITTED BY: A. R. HANKE

APPROVED BY : B. H. PERKINS

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## I. INTRODUCTION

The recently allowed Lane patent on "Copper-Phthalocyanine in Pigmentary Beta Form and Process of Making the Same", has made it desirable to obtain particle size distribution estimates with somewhat greater precision than can be had by a casual inspection of electron micrographs. This report records the results of particle size counts from electron micrographs of our BT-297-D SD 90497 and a typical sample of Calco's beta phase CPC coded C-53926, Cyan Blue 55-3300, Lot R-2924-109.

In any work designed to obtain a particle size distribution, it becomes necessary to attempt to define what is meant by a particle. For a great many powdered substances a consideration of the particle size of the pigment consisting of coarse lumps or cakes down to the very fine sub-microscopic fraction of the material, shows that there is some particle which requires considerably more energy to reduce its size than the other larger particles. This particle is usually termed the "ultimate" particle, although it should be recognized that the definition of ultimate particle is not a rigid one and an excessive change in the magnitude of the force of subdivision can finally cause a fracture of a so-called "ultimate" particle and a new "ultimate" particle must be defined.

Beta phase CPC of pigmentary quality is manufactured in such fashion that the small ultimate particle is a crystal fragment. That this is so, is evident from the manufacturing process, and the electron micrographs definitely show the crystalline nature of the pigment. The ultimate particle is therefore defined as this crystal fragment as it exists in the finished pigment. In speaking of particle size and particle size distribution, it is this crystal fragment that is meant and not some aggregate of crystal fragments capable of being broken down to the individual crystal fragments.

## II. SUMMARY AND CONCLUSIONS

1. Both Calco's product and our product have over 90% of their ultimate particles of a size less than 0.1$\mu$ average diameter.

2. There is an occasional particle greater than 0.2$\mu$ average diameter but it amounts to only 0.4% for our product and 0.1% for Calco's product.

3. An examination of the rectangular histograms definitely shows the similarity in particle size distribution between the two products, with our product containing somewhat more large particles than Calco's pigment.

4. Two average particle diameters derived from the distribution data and the average diameter calculated from a specific surface measurement further illustrate the similarity of the two pigments. The diameters in microns are given below:

| | BT-297-D | Calco's Cyan Blue (C-53926) |
|---|---|---|
| $d_1$ | 0.067 | 0.066 |
| $d_3$ | 0.100 | 0.083 |
| d (sp.surf.) | 0.061 | 0.062 |

Note:- The ave. dia. nomenclature is fairly well standardized throughout the literature, (ref.) but to avoid ambiguity, any average particle size diameter should always be defined.

$$d_1 = \frac{\sum nd}{\sum n}$$

$$d_3 = \frac{\sum nd^3}{\sum nd^2}$$

n = number of particles in a size class.
d = ave. diameter of each size class.

## III. EXPERIMENTAL TECHNIQUES

To obtain the particle size distribution of these crystal fragments it is necessary to disperse them to the degree where size measurements can be made on individual fragments, using the electron microscope to get the necessary magnification. Because of the smallness of the particles in question, to get adequate dispersion is a very difficult procedure in which is embodied the technique of trial and error.

It should therefore be understood that any written procedure is not to be considered as yielding unequivocally suitable electron micrographs, but, most usually, repeated attempts must be made in which modifications are employed as to the pigment particle population, the thickness of the film supporting the pigment dispersion, the length of time the sample is rubbed, how hard it is rubbed, how long the sample is allowed to stand in contact with the dispersing medium, etc. Experience coupled to a certain amount of luck will finally yield a dispersion from which it is possible to make particle size counts on particles which appear to be, for the most part, single particles. It must be realized, however, that at least some of these particles are probably aggregates and that a particle size count will give a distribution with averages somewhat larger than those given if it were possible to strictly measure single crystal fragments.

### A. Procedure for Preparing Electron Micrographs

A small amount of the dry pigment (± 10 mg) is mixed with about two drops of KV-36-TV*(approx. 20% nitrocellulose). This is rubbed on a Carrara glass suede finish plate using a small palette knife. The rubbing time is usually 5 minutes. Thinner is added from time to time to maintain a workable though heavy ink. A portion of the resulting ink is thinned with diluted nitrocellulose prepared by diluting the KV-36-TV with T-3601 in a ratio of 1 to 20. Such a dilution gives approx. a 1% nitrocellulose solution. This diluted ink is thoroughly mixed in with the palette knife.

*The composition of KV-36-TV is as follows:-

| | | |
|---|---|---|
| 1/4 sec. nitrocellulose (70% Solids) | - | 14.9% |
| 1/2 sec. nitrocellulose (70% Solids) | - | 14.9% |

*The composition of T-3601 is as follows:-

| | |
|---|---|
| Butyl Acetate | 37.0% |
| Toluol | 35.0% |
| Ethyl Acetate | 12.5% |
| Butyl Alcohol | 12.0% |
| Ethyl Alcohol (23A) | 3.5% |

/ Cararra glass is a structural glass manufactured by Pittsburgh Plate Glass Co. It comes in a gloss and a suede finish. The suede finish furnishes an ideal surface for intimately mixing pigment and vehicle with a palette knife.

One drop of this dispersion is placed on a clean microscope slide. The edge of another slide is used to smear the drop over the surface of the slide. The film so formed dries almost immediately and is floated on to water in a crystallizing dish by carefully inserting one edge of the slide into the water. The film will separate from the slide as the slide is further immersed until it finally floats free. It is well to score the film before floating it on to the water so that several isolated film sections will be floating on the water. A convenient scoring tool is a dissecting needle.

Since the edge of the slide used to spread out the drop is not perfectly straight but contains very small ridges, the film sections are not of uniform thinness and with experience a region of the required thinness can be selected and picked up on a 200 mesh screen 1/8" dia. In order to accomplish this, the 200 mesh screen, supported on a little brass platform equipped with a small handle, is taken below the surface of the water under the selected portion of the film. The screen is then raised so that it supports the selected film section. This follows the film mounting technique also applicable to preparing mounts for electron diffraction and is described in greater detail on p. 8 of KN-46-78. The screen containing the film is removed from the support and allowed to dry for a few minutes. It is then transferred to the electron microscope holder. Tweezers are used to facilitate this transfer. If the image on the fluorescent screen has poor resolution, it is probable that the film is too thick and another mount must be made selecting a thinner portion. If the film breaks even with a low intensity beam current, the film is too thin and a thicker portion must be selected. If considerable aggregation is evident, inadequate dispersion is indicated, and another ink must be prepared. More attention should be given to the rubbing stage of the technique, particularly after the final addition of dilute KV-36-TV. Also, in particularly stubborn cases, aging the ink for several days has been known to improve the dispersion. If the field is too thickly populated for easy viewing or too sparse to obtain a typical representation, the whole mounting procedure must be repeated, adjusting the quantity of pigment used.

In actual practice, several mounts are always made employing the variations mentioned above until a picture, or group of pictures, is obtained which show adequate dispersion for the purpose intended. If a particle size count is to be made, it is particularly important to have as highly a resolved image as is consistent with the practical

range of the microscope. The degree of dispersion must also be sufficient to allow the counting of enough single particles, avoiding the counting of aggregates as single particles.

B. Procedure for Particle Size Counting

The electron microscope yields a photographic negative 2 x 2" and with a magnification of approx. 6,000 X. The actual magnification calibration will be described in another section. This negative is optically projected on a screen making the projected magnification 50,000 X. Only the center portion of the negative is considered for counting in order to minimize the distortion introduced by optical aberrations. The projection size used for this work was 20 x 20 cm. The screen is cross-ruled to form rectangles to conveniently divide the counting field into smaller sections. A convenient degree of subdivision is eight sections of 5 x 10 cm each. Actually the size section most convenient will vary with the population density of the particle and any degree of subdivision may be used.

Inspection of the particle sizes will suggest a suitable size interval. For this work, the size intervals chosen were $> 0.40\mu$, $0.40\mu$ to $0.30\mu$, $0.30\mu$ to $0.20\mu$, $0.20\mu$ to $0.10\mu$, $0.10\mu$ to $0.05\mu$, and $< 0.05\mu$. The precision of measurement was assumed to be around $0.01\mu$.

To automatically obtain an average dimension for particles that are non-spherical in shape, linear measurements were made always in the same direction. This assumes random orientation and is an accepted technique recorded in the literature (ref.). The direction chosen is immaterial. For this work, measurements were made horizontally.

Care should be exercised in avoiding the counting of aggregates as single particles. There is no good rule to follow to completely avoid this and undoubtedly some aggregates will be counted as single particles. An accepted rule to follow is to not count a particle unless one can see at least half of its perimeter.

In actual practice the particles are measured with a pair of dividers, starting with the largest size range first. For this work very few particles exceeded $0.20\mu$ hence the first two classes could be counted and totaled more or less simultaneously. The next class, $0.20\mu$ to $0.10\mu$ is counted by setting the dividers at $0.1\mu$ and counting all particles $0.1\mu$ and over which have not been counted in the previous range. The dividers are then set at $0.05\mu$ and all particles $0.05\mu$ and over which have not been counted in the previous range are counted and at the same time all particles under $0.05\mu$ are also counted. This technique is, of course, applied to each of the subdividing rectangles. To avoid counting the same particle twice at the boundary line between adjacent rectangles, the particles touching only the left and upper sides are counted with each rectangle. This follows the accepted practice of blood cell counting. The sums for each rectangle are totaled to give the number of particles in each size class.

C. Procedure for Magnification Calibration

Two independent methods were used to obtain an absolute measure of the magnification. One method was to cast a nitrocellulose replica of a grating designed for this purpose and marketed by Baird Associates. This is a ruled grating with 15,000 lines to the inch making the distance between line centers 1.7 microns ± 1% apart. The replica is prepared by spreading a solution of nitrocellulose in amyl acetate over the grating and then floating it off on to water. This film is then picked up on a mounting screen in the conventional manner. The actual distance apart of the lines on the photographic negative measured with a cm. rule and expressed in microns divided by 1.7 microns gives the magnification factor for the electron microscope. Care must be exercised in maintaining the same conditions with regards to instrument magnification for both the grating picture and the pigment pictures. Of particular importance is the maintaining of a constant position of the "pole-piece" in the electron microscope. Even a slight change in its position can markedly change the magnification factor.

In spite of the seeming simplicity of this method, the mounting of a nitrocellulose film replica of the grating without introducing some distortion is practically impossible. A certain amount of shrinkage and distortion of the film upon drying is also a recognized source of error. Because of this, another independent method was also used to establish the magnification factor. This other method appears quite involved but actually it is felt to be more reliable than the grating method. The primary standard instead of being a grating is a light microscopic stage micrometer with lines 0.01 mm apart. A light photomicrograph of this stage micrometer is taken at a magnification of approx. 700 X. For this work, a 44 X objective with a 20 X Hyperplane ocular, and 18.2 cm tube length was used. The negative was a 4 x 5 inch Eastman 40 plate. The magnification factor for the light microscope is thus obtained by simply dividing the line distance on the photographic plate by the line distance of the lines on the stage micrometer. A light micrograph, at this magnification, is then taken of a hole in an electron microscope specimen screen. This hole is produced by enlarging one of the holes in a 200 mesh screen with a needle. Inspection of such a hole usually reveals enough rough edges and burrs to serve as measuring points for calibration purposes. A convenient measuring point is chosen large enough to measure on the 4 x 5 light micrograph negative but not so large that it will exceed the size of the field in the electron microscope when used at low power. The true size of this distance is obtained by dividing the measurement on the negative by this light microscope magnification factor. For the sake of illustration, call this distance "A". A low-power magnification electron micrograph negative of this distance is now obtained and the magnification factor of the electron microscope at low power is calculated by dividing the measured distance on the negative by "A". Inspection of this electron micrograph negative will reveal sufficient small structure large enough to make a measurement on the electron micrograph negative but small enough to lie within the field at high magnification. The true size of this smaller distance is obtained by dividing the distance as measured on the negative by the magnification factor of the electron microscope at low magnification. Call this distance "B". A photographic negative is now obtained of this region of the hole in the specimen screen and the magnification factor for the

electron microscope at high magnification is obtained by dividing the distance as measured on the negative by the distance "B". This is in the neighborhood of 6,000 X but must be redetermined by remeasurement of the image of "B" each time the pole-piece of the microscope is moved.

In actual practice it is advisable to make more than one measurement in each size range and average the resulting magnification factors. The overall precision of the magnification factor of the electron microscope is better than 5%. A typical comparison of the low power magnification factor using the two methods outlined above is 660 for the grating and 667 for the stage micrometer.

In projecting the photographic negative of a pigment dispersion under high magnification, the distance of the projector from the viewing screen is so chosen that the projected magnification is 50,000 X. It is at this magnification that the particle size count is made. A centimeter rule with half millimeter divisions is used to make the particle size measurements. The precision of the measurement is not fixed by the degree of subdivision of the rule, but is fixed by the uncertainty involved in defining the edge of the particle. If one assumes a precision of + 0.5 mm, an 0.1$\mu$ particle can be measured with a precision of 10%. This means that the magnification factor contains less error than the final particle size measurement. A fair estimate of the overall precision in particle size measurement is therefore 12%.

D. Data for BT-297-D and Calco's Cyan Blue

Four electron micrographs with dispersions suitable for counting were obtained of BT-297-D and are illustrated in Figures 1, 2, 3, and 4. The actual particle size count is shown in Table I.

Two electron micrographs with dispersions suitable for counting were obtained of Calco's Cyan Blue and are illustrated in Figures 5 and 6. The particle size count is shown in Table II.

Figures 7 and 8 are rectangular histograms of BT-297-D and Calco's Cyan Blue respectively plotting particle frequency against size class using the grand totals shown in Table I and II. Table III shows the pertinent statistical data which well illustrate the similarity between our sample and Calco's sample. Specific surface measurements were made on the two samples at the Experimental Station using the nitrogen adsorption technique. These data are also given in Table III.

## TABLE I

### PARTICLE SIZE DISTRIBUTION FOR BT-297-D SD 90497

| Fig. No. | Plate No. | SIZE CLASS TOTALS (SIZE EXPRESSED AS AVE. DIAMETERS) >0.40μ | 0.40-0.30μ | 0.30-0.20μ | 0.20-0.10μ | 0.10-0.05μ | <0.05μ* | Plate Totals | Total <0.10μ | % <0.10μ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1471 | 0 | 0 | 1 | 43 | 592 | 474 | 1110 | 1066 | 96.1 |
| 2 | 1291 | 0 | 0 | 3 | 85 | 227 | 88 | 403 | 315 | 78.2 |
| 3 | 1457 | 0 | 0 | 4 | 17 | 192 | 181 | 394 | 373 | 94.6 |
| 4 | 1458 | 0 | 1 | 0 | 35 | 292 | 275 | 603 | 567 | 94.0 |
| Grand Totals | | 0 | 1 | 8 | 180 | 1303 | 1018 | 2510 | 2321 | 92.4 |
| | | .000 4 | | 9 | 18⁰ | 189 | 1402 | | | |
| | | | | .0036 | 754 | 1492 | 2510 | | | |
| | | | | | | 595 | | | | |

## TABLE II

### PARTICLE SIZE DISTRIBUTION FOR CALCO'S CYAN BLUE (C-53926)

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 5 | 1468 | 0 | 0 | 0 | 16 | 539 | 266 | 821 | 805 | 98.0 |
| 6 | 1467 | 0 | 0 | 1 | 24 | 382 | 188 | 595 | 570 | 96.0 |
| Grand Totals | | 0 | 0 | 1 | 40 | 921 | 454 | 1416 | 1375 | 97.0 |

* The class<0.05μ was difficult to measure because of its small size. It was obvious by inspection of the micrographs that most of the particles in this class were close to 0.05μ in size, hence an estimated average of 0.04μ was used for this size class. For all other size classes, the arithmetic mean of the size class limits were used as the particle size of each class.

TABLE III

STATISTICAL SUMMARY

| | BT-297-D | Calco's Cyan Blue |
|---|---|---|
| Total No. of particles counted | 2,510 | 1,416 |
| Particles no greater than 0.1 micron ave. dia. | 92.4% | 97.1% |
| Particles in the range 0.1 micron to 0.2 micron ave. dia. | 7.2% | 2.8% |
| Particles greater than 0.2 microns ave. dia. | 0.4% | 0.1% |
| Ave. particle dia. "$d_1$" (microns) | 0.067 | 0.066 |
| Ave. particle dia. "$d_3$" (microns) | 0.100 | 0.083 |
| Ave. particle dia. calc. from specific surface (microns) | 0.061 | 0.062 |

The average diameters $d_1$ and $d_3$ were calculated from the data in Tables I and II using the following formulas:-

$$d_1 = \frac{\sum nd}{\sum n}$$

$$d_3 = \frac{\sum nd^3}{\sum nd^2}$$

n = number of particles in a size class.
d = ave. diameter of each size class.

The nomenclature followed is that generally found in the literature (ref.). The average diameter "$d_1$" is called "Mean diameter". The average diameter "$d_3$" is called "Mean volume-surface diameter". This "$d_3$" diameter is the same type of average as that obtained directly from a specific surface measurement.

In Table III, the average diameters calculated from specific surface measurements were calculated from the formula:-

$$d_{sp.\ surf.} = \frac{6}{Sp.Surf. \times Sp.Gravity}$$

sp. surf. = Diameter expressed as microns
Sp. Gravity = 1.54
Sp. Surf. expressed as sq. meters per gram

## III. DISCUSSION

There is a definite similarity between the two pigments with Calco's product containing a somewhat larger percentage of small particles than our pigment. As expected, the two averages $d_1$ and $d_3$ are not in agreement. The $d_1$ average favors the smaller particles, hence its value will be lower than the $d_3$ average. The $d_3$ average is of the type calculated from specific surface data but the agreement between $d_3$ and that calculated from specific surface is not particularly good. It is felt that the biggest single factor responsible for the lack of agreement is the extreme difficulty of avoiding the counting of loose aggregates as single particles. The nitrogen molecule does not have this difficulty and hence indicates a smaller average diameter. The resolving power limit of the microscope is also a factor which will tend to give a measurement larger than the true size. The closer the particle diameter is to the resolving power of the instrument, the greater will be the error. The resolving power of the microscope is probably around 0.01$\mu$. This is still a five-fold factor below the 0.05$\mu$ particle size which is probably close enough to have some effect but not as great an effect as the counting of aggregates as single ultimate particles.

## IV. FUTURE PROGRAM

It is planned to obtain particle size distribution data on other pigments as time permits.

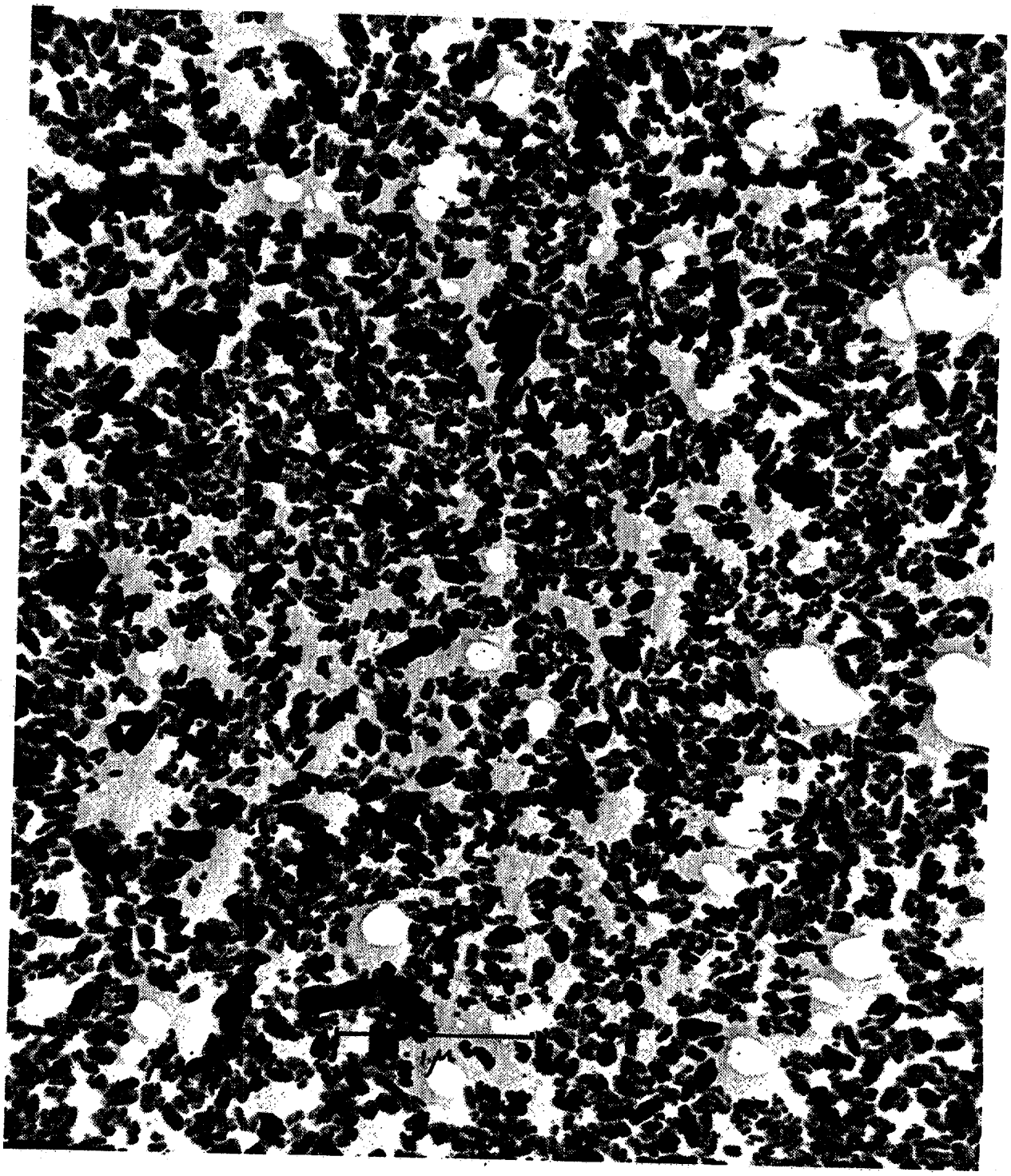
## V. REFERENCES

E. K. Fisher "Colloidal Dispersions", John Wiley & Sons Inc. New York 1950.

The experimental work is recorded in NB-1137-76 & 77.

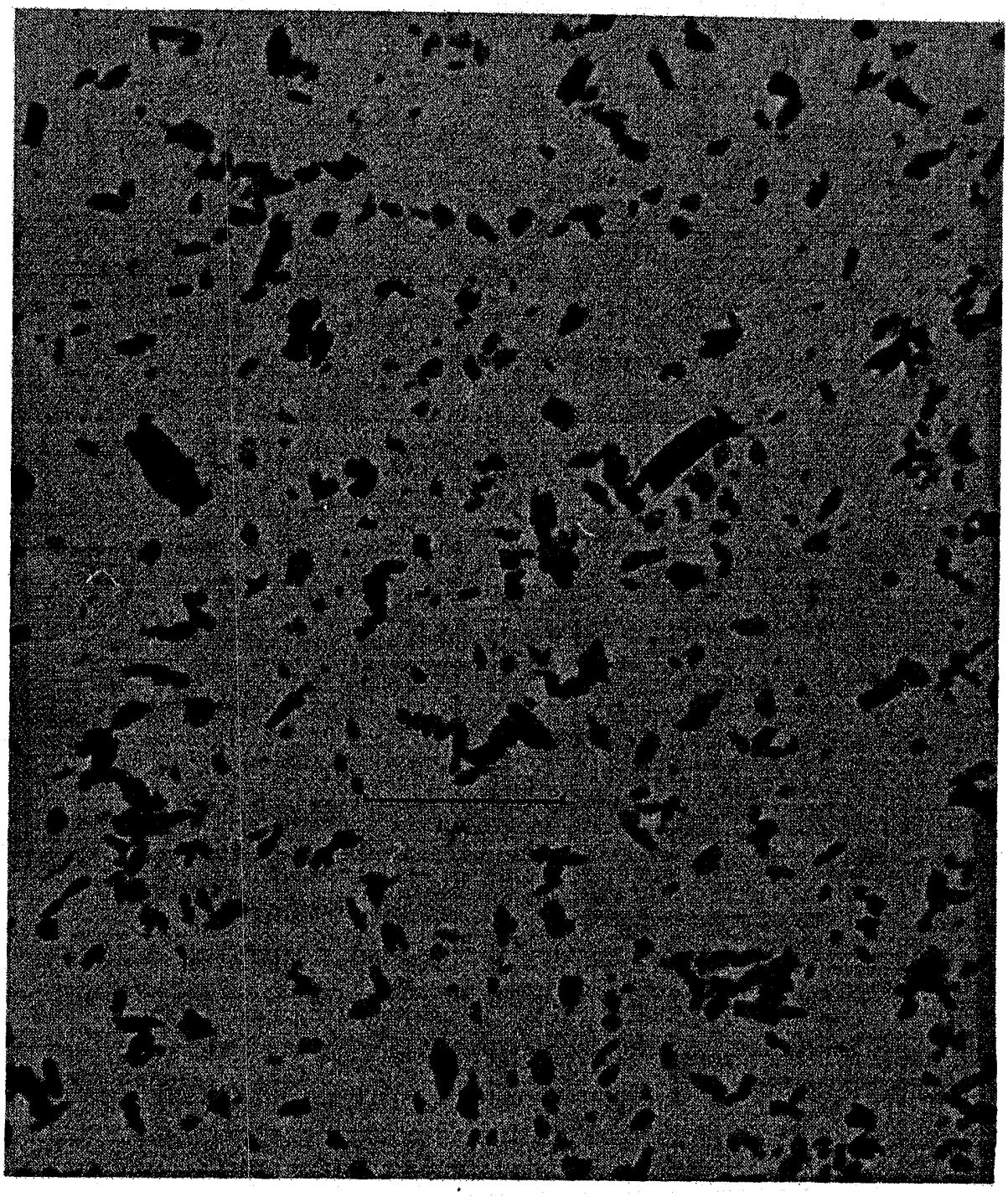
ARH:lg

Figure 1. BT-297-D, SD-90497. Plate 1471



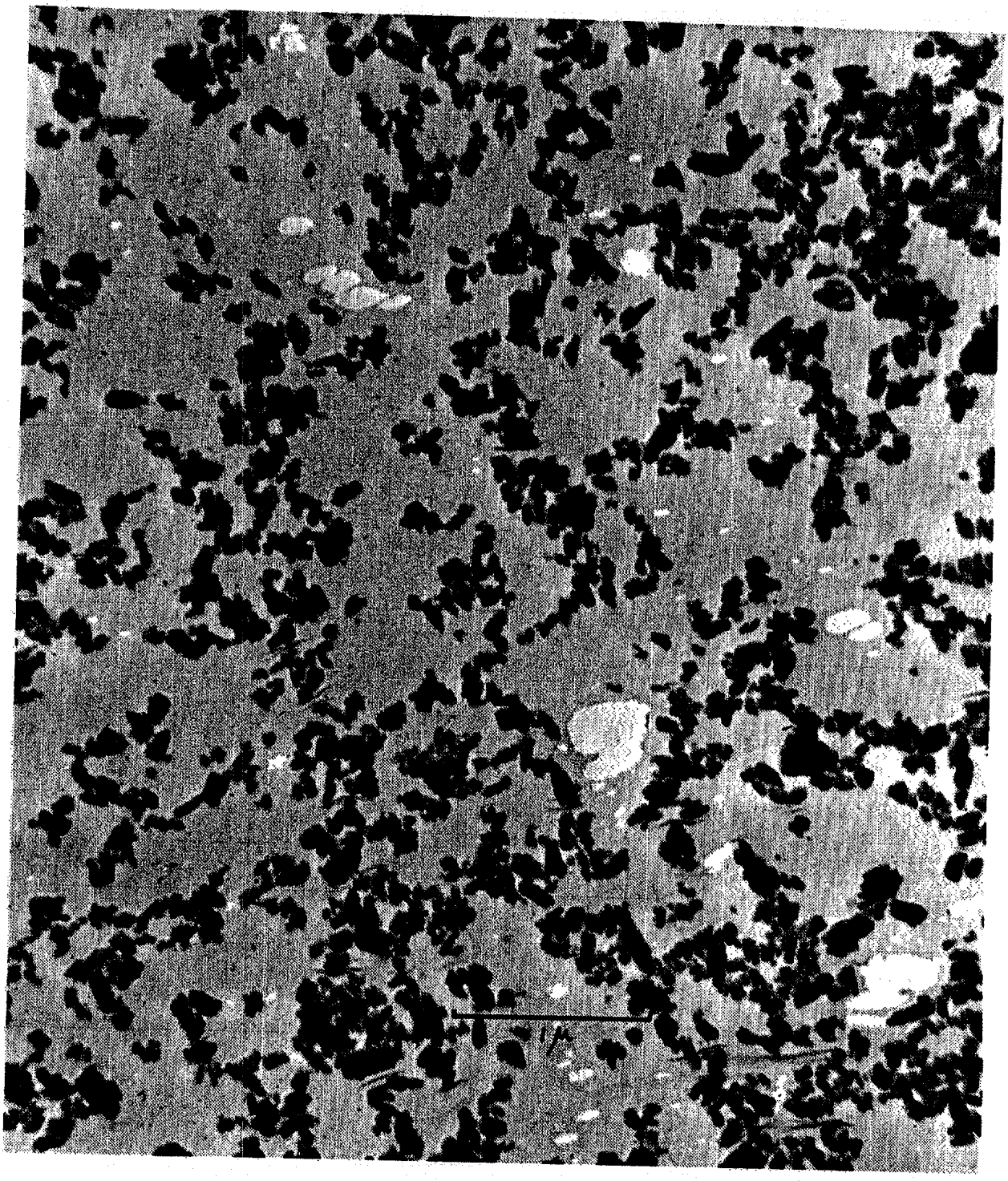
35,000 X

Figure 2. BT-297-D, SD-90497 Plate 1291



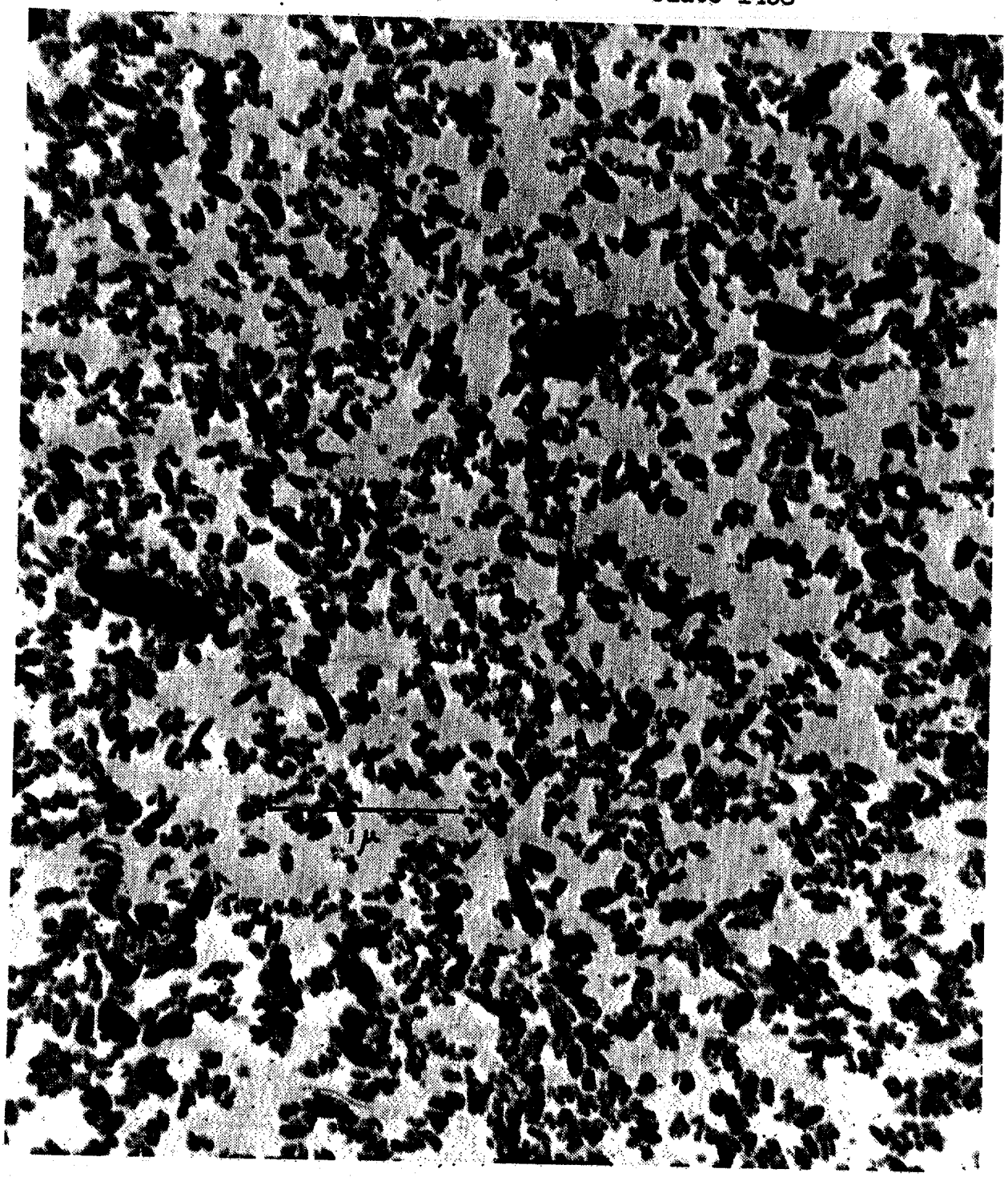
35,000 X

Figure 3. BT-297-D, SD-90497 Plate 1457



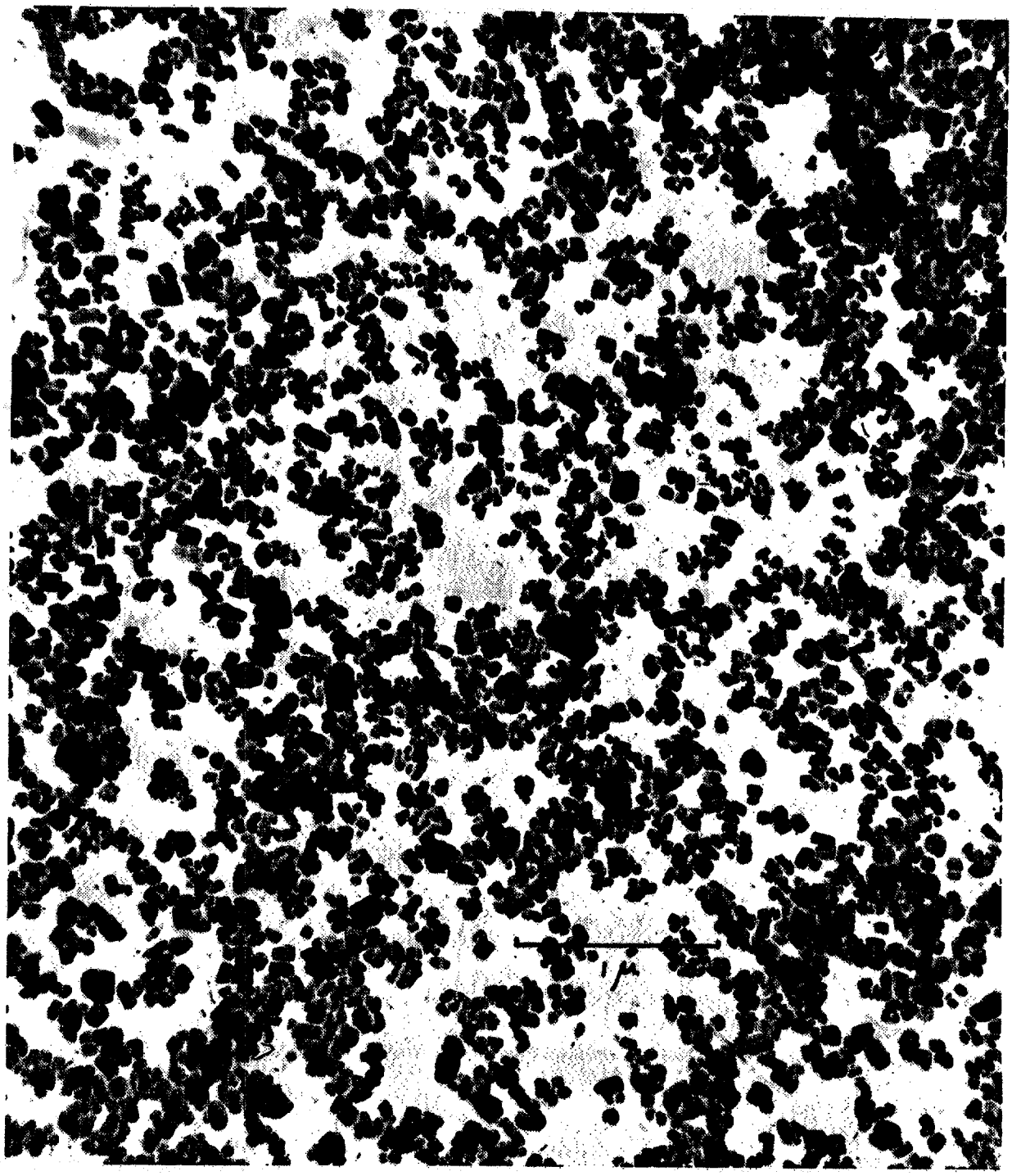
35,000 X

Figure 4. BT-297-D, SD-90497 Plate 1458



35,000 X

Figure 5. Calco's Cyan Blue, C-53926. Plate 1468




35,000 X

Figure 6. Calco's Cyan Blue, C-53926 Plate 1467


35,000 X

FIG. 7 BT-297-D SD-90497

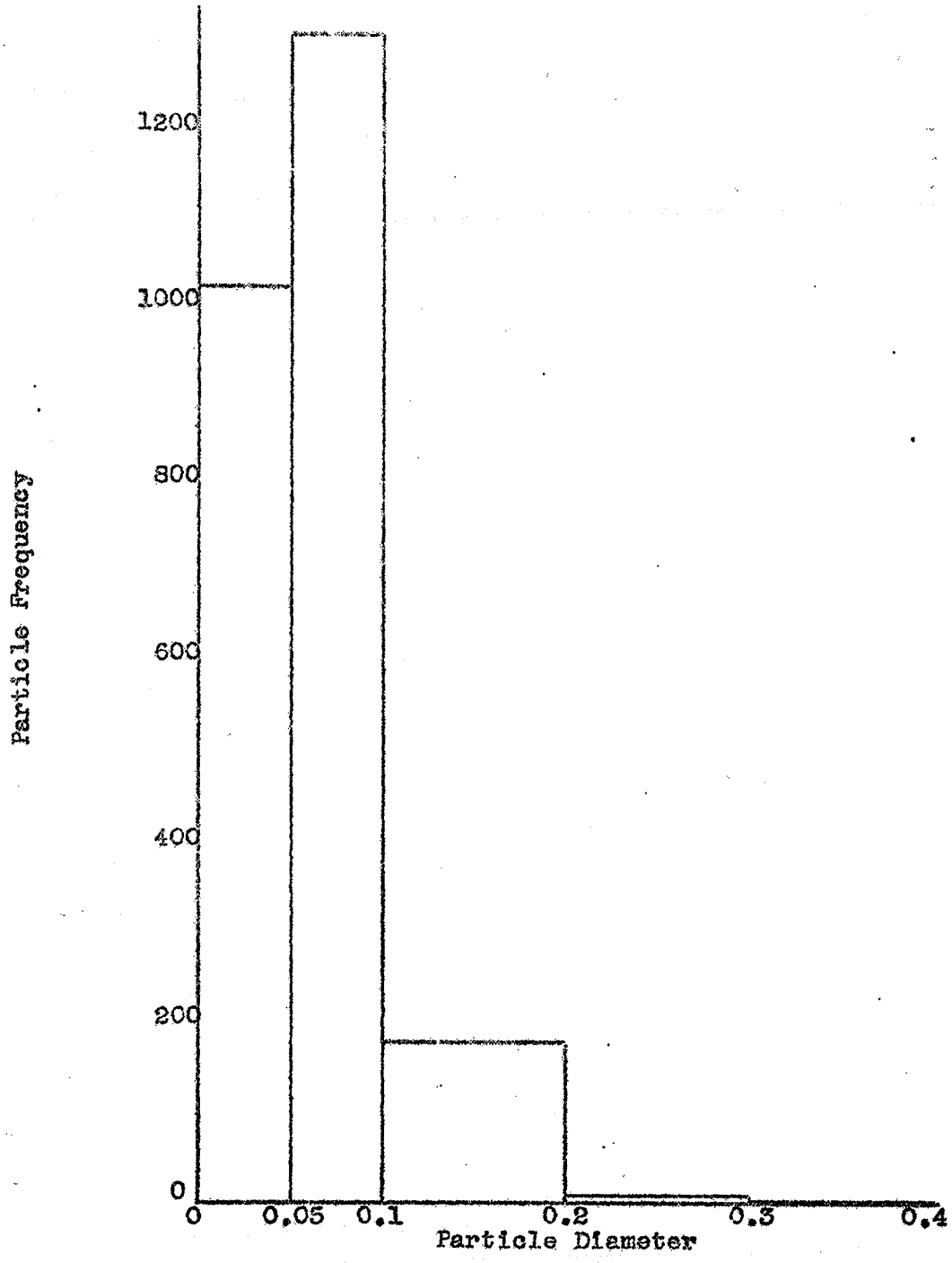
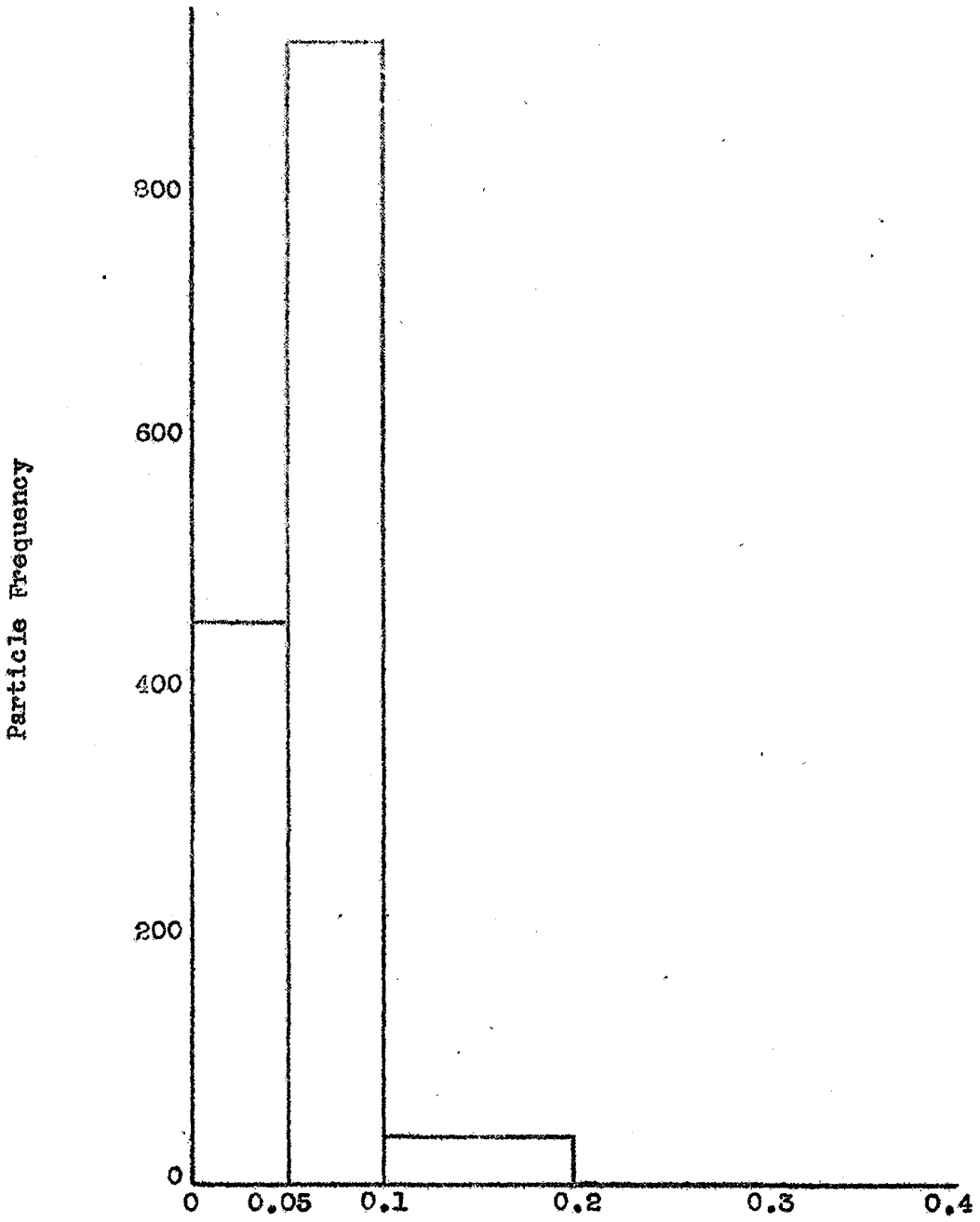
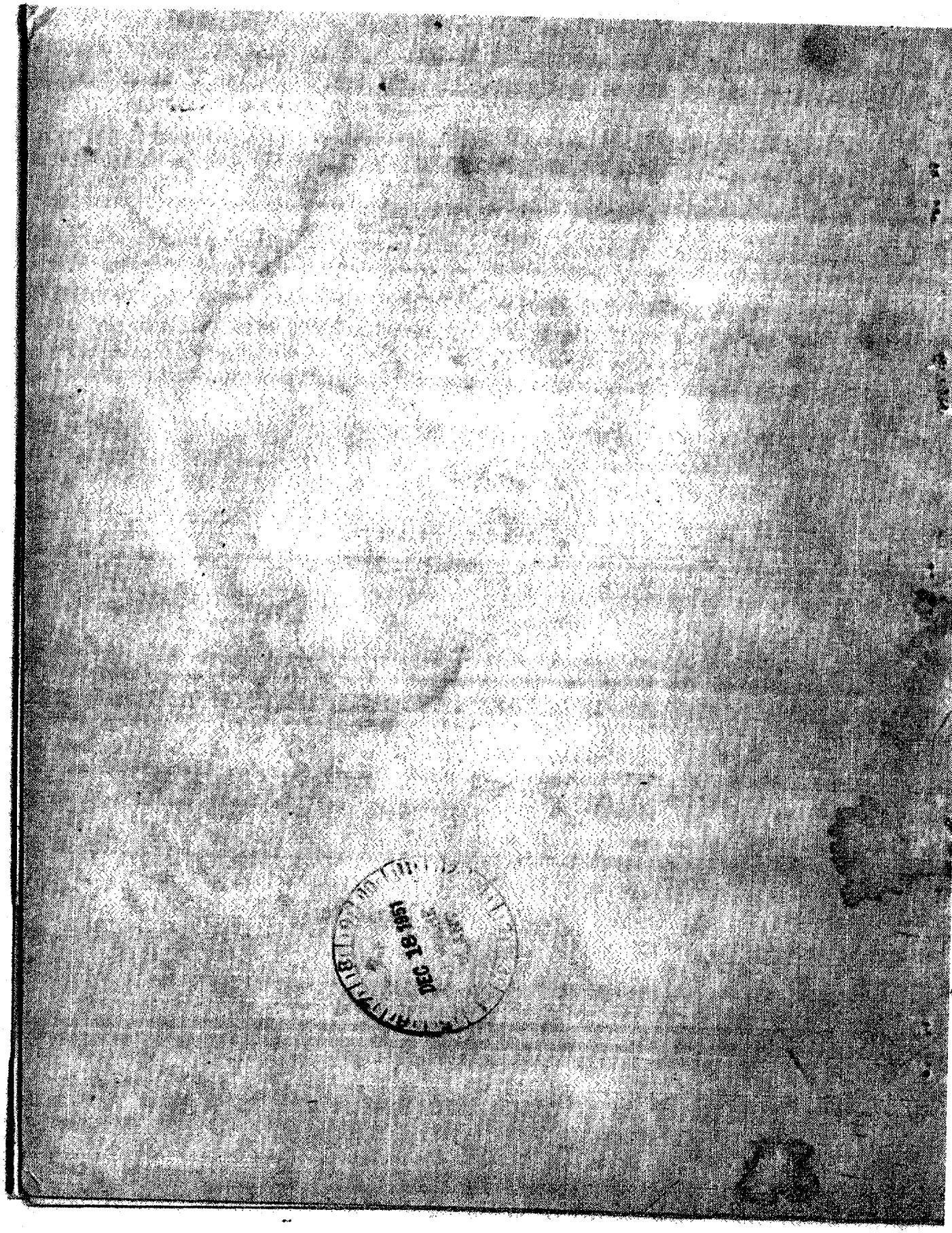
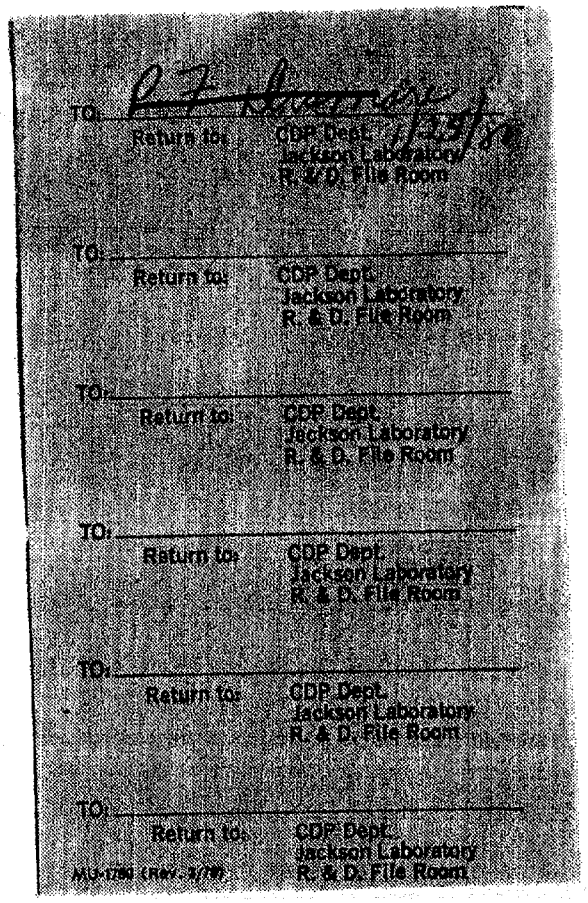


FIG. 8 CALCO'S CYAN BLUE C-55926







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