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I hereby recommend that the thesis prepared under my supervision by Robert Benemelis

entitled Factors Influencing the Drying Properties of Printing and Lithographic Inks

be accepted as fulfilling this part of the requirements for the degree of Doctor of Philosophy

Approved by:

G. George

Hoke S. Greene

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FACTORS INFLUENCING THE DRYING PROPERTIES OF PRINTING AND LITHOGRAPHIC INKS.

A dissertation submitted to the

Graduate School
of the University of Cincinnati

in partial fulfillment of the
requirements for the degree of

DOCTOR OF PHILOSOPHY

1947

by

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18, 8, 47 am

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Cincinnati, Ohio
June 30, 1946

Graduate Faculty
Graduate School
University of Cincinnati
Cincinnati, Ohio

Gentlemen:

I herewith submit a dissertation entitled, "Factors Influencing the Drying Properties of Printing and Lithographic Inks" in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

The purpose of this investigation was to acquire more information regarding the factors controlling the drying properties of printing and lithographic ink. This problem is one of the most critical in the graphic arts industry.

Parts of this thesis have been published in Research Bulletin No. 13 of the Lithographic Technical Foundation.

Very truly yours,

Robert L. Benemelis

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INTRODUCTION

The drying of printing and lithographic inks has been for many years one of the most critical problems in the graphic arts industry. The drying properties of printing ink are extremely varied and slight changes in formulation, pigment, paper, temperature, and humidity have a marked effect. Considerable practical information has been acquired by printing ink formulators and pressmen, but until recent years, little fundamental research had been done on the subject.

A printing ink consists of the vehicle, whose function is to bind the pigment to the paper, the pigment which gives the ink its color and opacity, and the drier which enables the ink to dry within a practical length of time. Numerous additives are frequently used to improve the working properties of the ink.

Printing ink vehicles generally consist of bodied linseed or tung oils, modified phenolic resins, or modified alkyd resins. By far the most common vehicle is bodies linseed oil. The linseed oil after extraction from flax seed is alkali refined, and then bodied in covered, carbon dioxide blanketed copper or stainless steel vessels at a temperature of about 450°F. This proceedure produces the vest varnishes of this type. Frequently, however, cheaper grades of varnish are made by simply bodying the oil in open containers or by blowing the heated oil with air.

If harder varnishes are desired, as in the tin printing field, modified phenolic or alkyd resins are used. Modified phenolic vehicles are frequently made by adding para phenyl phenol resin to the cold oil and heating until the resin is disolved and the varnish has attained the desired body. Para phenyl phenol and bis phenol are the only common non-rosin phenolic resins that can be used in making phenolic varnishes. This is due to the fact that they are the only phenolic resins soluble in drying oils; a property acquired by blocking the active para position of the phenol molecule with a phenyl group thus preventing the formation of an oil insoluble, three dimensional polymer.

Addition of phenolic resin to linseed oil in this manner has the advantage of producing a harder, more rapidly drying varnish with the disadvantage of slightly darkening the color of the varnish.

The modified alkyd type varnish is rapidly coming into more general use because of its superior drying properties, its hardness, and its water-white color. This type of varnish is made by adding two moles of glycerol to one mole of linseed oil and heating the mixture in the presence of .1% litharge as a catalyst until the alcoholysis is complete. From 10 to 20% of phthallic anhydride is then added to the monoester and the mixture is held at approximately 180°C until the desired acid number and body are obtained.

The pigments used in printing inks are generally strongly colored salts of organic dyestuffs. A common method of making pigments is to select brilliant azo dyes with an available sulfonic acid group and to precipitate the insoluble calcium or barium salt of the dye. The lithol red colors are examples of this type of pigment. In recent years the phosphotungstated and phosphomolybdated triphenyl methane dyes have come into general use. These dyes are prepared by precipitating the basic triphenyl methane dye with phosphotungstic or phosphomolybdic acid. These colors are very brilliant and strong. The phosphotungstate of methyl violet, victoria blue, and malachite green are perhaps the best example of this type of pigment. The most recent class of pigments to come on the market is the phthallocyanine group. These colors are made by treating phthallonitrile with cuprous oxide or chloride. The product obtained is copper phthallocyanine, a brilliant blue pigment. Phthallocyanine green is made in the same manner except a brominated phthallonitrile is used. The only inorganic pigments of importance are titanium dioxide, chrome yellow, prussian blue, and carbon black.

The driers used in printing inks are now almost exclusively the naphthenates of cobalt, lead, and manganese. They are made by treating the oxides of these metals with naphthenic acid.

obtained from petroleum. They are decidedly superior to the resinates and linolates because of their greater solubility in drying oils.

The drying of printing and lithographic inks has been the subject of observation and study by the printing ink industry for many years. It is generally accepted that drying is a result of about three processes: penetration, oxidation, and polymerization. Undoubtedly all these processes are taking place at the same time in varying degrees depending upon the particular drying conditions.

In this investigation drying by penetration was not considered a true drying mechanism and no attempt was made to study its effect. It consists in absorption of the vehicle into the paper, leaving an ink film of high concentration of pigment at the surface which does not "set-off" and which is considered dry. It should be noted that this process does not cause true drying, but it is quite probable that it facilitates drying by oxidation and polymerization. This phase of the problem has been previously investigated.[1]

Drying by oxidation is quite evident from the fact that a drying oil gains weight when exposed to an atmosphere containing oxygen. Peroxides are known to be present during the first stages of drying, and it is generally believed that they act catalytically in transfering the oxygen from the air to the oil molecule. The iodine number of the oil decreases during drying which indicates that oxidation takes place at the double bonds and that drying tends to saturate the oil molecule. Oils with a greater number of conjugated double bonds dry more rapidly. Sunlight, ultraviolet light, heat, and ozone are known to accelerate drying.

The mechanism by which oils dry by polymerization is little understood. It is known that when the temperature of oil is increased in the absence of oxygen, its molecular weight will increase, and if the heating is prolonged it will solidify. The molecular weight of an oil greatly increases during normal drying indicating that polymerization takes place.[2] In tung oil, where there exists a system of conjugated double bonds, polymerization takes place at a more rapid rate, a hard film is produced, and there is evidence that cross linking at the double bond takes place producing a three dimensional polymer. Numerous mechanisms by which this may take place have been proposed, but the most satisfactory theory is that the conjugated double bond system reacts with one double bond of a second oil molecule by 1-4 addition, producing a ring structure.[3] The remaining double bond of the first oil molecule reacts again with another conjugated pair of double bonds by the same method, producing a second ring that is fused to the first ring. In these mechanisms the role of oxygen, or of peroxides formed by the addition of oxygen to the double bond, is purely that of a catalyst. In linseed oil, which does not have a conjugated double bond system, there is no evidence that cross linking takes place. There is evidence that polymerization can be accelerated by lead driers and stannic chloride.[4]

When oxidation and polymerization have reached a certain stage, the ink vehicle becomes extremely viscous and rather suddenly is transformed from the liquid to the solid "gel" state. This "gel" state has sufficient strength to prevent "set-off" and can be readily handled.

Since drying oils do not dry rapidly enough by themselves for practical purposes, driers must be added. As has been mentioned previously, driers are generally salts of cobalt, manganese, and lead. Drier action is believed to be catalytic in that it facilitates the transfer of oxygen from the atmosphere to the oil molecule. There is evidence, however, that driers are not true or perfect catalysts since the acid radical with which the metal is combined has a decided influence on the effectiveness of the drier.[5] The explanation offered is that the drier metal must be readily available and some acid radicals decrease the availability of the metal more than others.

There are a great many factors which affect the drying of printing inks. One of the most important of these is the nature of the pigment. Pigments may inhibit or accelerate drying. The pigment may accelerate drying by oxidizing the oil molecule. It has been observed that a film of ink pigmented with chrome green, when allowed to dry in the absence of air will decolorize due to the reduction of the pigment.[6] Pigments containing iron and chromium are believed to be oxidizing.

The pigment may also react with the vehicle to produce drying soaps. This is undoubtedly the case when alkaline pigments such as the alumina hydrate lakes are used. The majority of pigments, however, are too inert to react in this manner.

Pigments also adsorb drier on their surfaces. This action is most pronounced with carbon black which adsorbs more drier than any other pigment and is consequently the most difficult to dry.[7] Other pigments adsorb drier to a lesser extent.

Temperature and relative humidity also strongly influence the drying of inks. An increase in temperature decreases the drying time, whereas an increase in relative humidity greatly increases the drying time. It is well known that increased temperature increases the rate of any chemical reaction, and since drying is a process involving oxidation and polymerization it is not surprizing that increased temperature increases the drying rate. The effect of humidity is not as yet understood. There is, however, some evidence to indicate that the effect of humidity is due to the presence of the pigment particles. Increased humidity appears to have no effect on the drying time of unpigmented films.

THE NATURE OF THE PROBLEM

The work upon which this thesis is based was done with the intention of acquiring a better understanding of the many factors which influence the drying of printing inks. Specifically, an attempt was made to study the effect of coating pH, of pigment pH, of different types of pigments, and of pigment particle size. Some of this work represents a continuation of the work done at the Lithographic Technical Foundation by Dr. Cadwell and the author.

Although the effect of different kinds of paper on ink drying time has been investigated, no data has been published on the effect of the coating pH.[7] Since it is known that the pigment pH affects drying time it is reasonable to suppose that coating pH would also affect drying time.

The effect of pigment pH on ink drying time has been mentioned in the literature. Bennett[6] summarizes much of the theory of earlier work in his generalization that alkaline pigments accelerate drying because of soap formation. This theory, however, has found much less favor in recent years. S. Marks[8] observed the accelerating effect of alkaline pigments and advanced the theory that alkaline pigments and not acidic pigments so orient the drying oil molecules on their surfaces that the unsaturated part of the molecule is readily accessible to atmospheric oxygen. W.B. Wiegand[9] discovered during his study of the properties of carbon black pigments that high pH carbon blacks facilitate drying whereas low pH carbon blacks retard drying. O.J. Brown and W.R. Smith[10] observed in a study of the drying properties of printing inks formulated with different types of carbon black pigments, that the alkaline pigments accelerated drying while the acidic pigments retarded drying. Some data is also available to indicate that pigments made by acidic processes frequently retard drying.

The large variance in the drying properties of inks formulated with different types of pigment has long been known. Bennett[6] concludes that pigments may influence drying in four different ways. They may:

1. take part in the oxidation process;
2. remove drier from the vehicle;
3. promote changes in the structure of the vehicle;
4. interact to produce soaps.

Rhodes and Van Wint[11] found that certain pigments have a marked effect upon the rate of oxidation of the vehicle. Zinc oxide, barium sulfate, and titanium dioxide decrease the rate and extent of oxidation of the vehicle. White lead increases the rate of oxidation of the vehicle. Many pigments, however, have no effect. Gardner[12] found that many pigments remove drier from solution in the ink vehicle. Carbon black is an excellent example of this type of pigment. D.H. Clewell[13] found that some pigments, generally basic, had a pronounced effect on the orientation of molecules; the polar groups, in many instances, were drawn toward the pigment surface. Venetian red is a good example of this type of pigment.

The effect of pigment particle size on the drying properties of printing inks is a very new field and very little experimental data has been acquired to date. In fact the only work that has been done on this subject is confined to carbon black pigments. O.J. Brown and W.R. Smith[10] have studied the effects of various carbon black pigments varying in particle size on the drying properties of an alkyd resin vehicle. They conclude from this work that ink drying time increases with decreasing particle size. Except for the experimental work reported in this thesis, this study is the only published attempt to relate ink drying time with pigment particle size.

Until recent years there has been only a slight interest in determining the particle size and surface area of particles in the subsieve range. With the invention and development of the electron microscope, however, an intense interest has develped in this field, and printing ink and protective coating chemists are inclined to explain many of the properties of ink and paint in terms of pigment surface area.

Numerous methods of determining the specific surface and particle size of pigments have been advanced. Upon practical application, however, the majority of these have serious shortcomings which severely limit their effectiveness. An attempt was made in this work to study all promising methods in the hope of finding an accurate, rapid, and relatively simple method.

EXPERIMENTAL WORK

The experimental work can be divided into five different parts as follows:

1. Effect of paper coating pH on ink drying time.
2. Effect of different pigments on ink drying time.
3. Effect of pigment pH on ink drying time.
4. Determination of pigment particle size and surface area.
5. Effect of pigment particle size on ink drying time.

1. Effect of pH of Paper Coating on Ink Drying Time

For this part of the experimental work a series of coated papers was prepared by The Champion Paper and Fibre Company. The pH of the coating slip varied from 7.3 to 10.0. A typical clay coating slip having a casein content of 16 per cent and a pH value of 7.3 was divided into four parts which were then adjusted to different alkalinities by the addition of sodium carbonate. The final pH values obtained were 7.3, 8.0, 8.9, and 10.0 respectively. These adjusted slips were coated on the same body stock by means of a laboratory coating machine, dried, and calendered.

Four different commercial lithographic inks were used and their drying properties studied on this series of coated papers. The formulations of these inks are given in Table I. Each ink was printed on each type of paper and the respective drying times determined in duplicate at three different relative humidities. The method of determining ink drying times at different humidities is completely described in reference 7.

It should be noted here that part of this work was done at a previous date and reported in reference 1. It was thought best, however, to incorporate all the data together so as to present a complete picture of this phase of the work. This data has also been published in the Lithographic Technical Foundation Bulletin No. 13.

The results of this work are tabulated in Tables II and III. These results show conclusively that the pH of the paper coating has a decided effect on the drying rate of the printing ink. In general, the greater the alkalinity of the paper coating, the shorter the drying time of the ink. The effect appears to be quite general and although more pronounced with respect to inks pigmented with carbon black, it is still marked with inks formulated with other pigments.

The effect of the coating pH on ink drying time becomes more pronounced as the relative humidity increases. It will be noted in Table II, ink No. 1, that at 92% relative humidity, only the paper of pH 10 dried within 24 hours. In general, the drying time of both inks pigmented with carbon black at a pH of 10 were doubled when put onto paper of pH 7.3. The extremely long drying time recorded for inks No. 3 and 4 on paper of pH 10 in Table III are unquestionably in error because of the"powderyness" of the coating at this humidity. It was noted during the preparation of these printed papers that those of pH 10 had a very fragile coating which "picked" badly.

There are three theories which might be offered to explain this phenomena:

1. The alkalinity of the paper coating may neutralize to a slight extent the free fatty acid present in the printing ink vehicle, producing solid soaps which by altering the consistency of the ink allow it to obtain a non-offsetting condition more rapidly than an ink without this neutralization. This effect is undoubtedly very slight, but when the small amount of ink applied to the paper, and its large surface are considered, it does not seem unreasonable to assume that this action may promote more rapid drying. This theory, however, has gone increasingly out of favor in recent years.

2. The alkalinity of the paper coating may catalytically accelerate the polymerization of the drying oil. This action is well known in many organic processes. It should be emphasized again that the number of square centimeters of ink surface per gram of ink is very large, a fact which suggests catalytic action.

3. The alkalinity of the paper coating may act as an orienting force by which the polar parts of the oil molescules are drawn to the surface of the paper thus placing the unsaturated parts

of the oil molecules in close conjunction, and thereby facilitating the drying processes of polymerization and oxidation.

The conclusions that may be drawn from the experimental drying data discussed here are:

1. The greater the pH of the paper coating, the more rapid the drying rate of the printing ink.

2. The greater the pH of the paper coating, the less the retarding effect of increased relative humidity on the drying rate of the ink.

TABLE I

FORMULATIONS OF PRINTING INKS USED TO DETERMINE THE EFFECT OF COATING pH ON INK DRYING TIME

Ink No.	Formulation	
1.	Sinclair & Valentine Ace Black	-90%
	Sinclair & Valentine #3 Varnish	- 5%
	Cobalt naphthenate drier containing 6% cobalt as metal	- 5%
2.	I.P.I. Offset Black Ink	-90%
	Sinclair & Valentine #3 Varnish	- 5%
	Cobalt naphthenate drier containing 6% cobalt as metal	- 5%
3.	Sinclair & Valentine Primrose Yellow Ink	-99%
	Lead and manganese naphthenate drier containing 2.6% manganese and 13.1% lead as metal	- 1%
4.	Sinclair & Valentine Violet Toner	-97%
	Cobalt naphthenate drier containing 6% cobalt as metal	- 3%

TABLE II

EFFECT OF PAPER COATING pH ON INK DRYING TIME

Ink No. 1

Papers	pH of coating slip	Drying Time in Hours at various Relative Humidities (R.H.) 43% R.H.	59% R.H.	80% R.H.	92% R.H.
1.	10.0	2.6	2.3	3.1	17.7
2.	8.9	2.6	2.3	4.9	34 +
3.	8.0	3.3	2.8	4.9	34 +
4.	7.3	3.2	4.1	8.5	34 +

Ink No. 2

Papers	pH of coating slip	Drying Time in Hours at various Relative Humidities (R.H.) 43% R.H.	59% R.H.	80% R.H.	92% R.H.
1.	10.0	2.0	1.8	3.2	17.1
2.	8.9	2.2	3.7	4.1	16.7
3.	8.0	2.9	3.7	6.7	20.0
4.	7.3	4.1	4.0	7.6	34 +

TABLE III

EFFECT OF PAPER COATING pH ON INK DRYING TIME

Ink No. 1

Papers	pH of coating slip	Drying Time in Hours at various Relative Humidities(R.H.) 42% R.H.	62% R.H.	82% R.H.
5.	10.0	1.1	1.1	1.3
6.	8.2	1.7	1.9	2.3
7.	8.0	2.7	3.3	12.7

Ink No. 2

Papers	pH of coating slip	Drying Time in Hours at various Relative Humidities (R.H.) 42% R.H.	62% R.H.	82% R.H.
5.	10.0	1.4	1.2	1.3
6.	8.2	2.1	2.4	3.6
7.	8.0	2.7	3.4	18.8

(continued on next page)

TABLE III (continued)

EFFECT OF PAPER COATING pH ON INK DRYING TIME

Ink No.3

Papers	pH of coating slip	Drying Time in Hours at various Relative Humidities (R.H.)		
		42% R.H.	62% R.H.	82% R.H.
5.	10.0	5.6	5.0	19.9
6.	8.2	5.7	6.7	5.7
7.	7.3	7.1	11.1	14.7

Ink No. 4

Papers	pH of coating slip	Drying Time in Hours at various Relative Humidities (R.H.)		
		42% R.H.	62% R.H.	82% R.H.
5.	10.0	1.8	1.9	22 +
6.	8.2	1.7	2.2	3.8
7.	7.3	2.5	2.6	3.6

2. Effect of Different Pigments on Ink Drying Time

This part of the experimental work was an attempt to determine the effect of different types of pigments on the drying properties of printing ink. As has been mentioned earlier, it has been known for many years that different pigments affect the drying properties of printing ink to a rather large extent. There is, however, little evidence that any organized study has been put on this subject. For this reason, it was decided to select fourteen pigments that are commonly used and which represent the different classes of pigments available. Sinclair & Valentine No. 3 varnish was used in each case and sufficient pigment added to make an ink with a tack of about 25 gram meters as measured on the Inkometer at 400 r.p.m.. Cobalt naphthenate drier containing 6% cobalt as metal was added to portions of each ink to make drier concentrations of .5, 1, and 2% drier, calculated on the weight of the varnish present. Inks of each drier concentration were run at relative humidities of 40, 60, and 76%. Duplex Super Varnish paper was used. The drying rate of each ink without drier was determined at a relative humidity of 40%. This work was repeated in part using lead and manganese drier. The composition of each ink is given in Table IV.

The comparison of different pigments by formulating them into inks of equal tack would appear at first glance to be faulty. However, when the method of applying the ink to the paper is considered, it is evident that the tack of the ink is the physical property which determines the thickness of the resulting ink film. It will also be seen that pigmentation to constant tack corresponds to pigmentation by volume. This is to be expected since tack is related to viscosity. Therefore, since pigmentation by volume would compare effective amounts of pigment, and since pigmentation to constant tack approximates this while also satisfying the requirements of the method of application, it is believed to be the best method of comparing a series of pigments.

The results of this work are given in Tables V and VI, and in Fig. 1. These results show rather pointedly that different types of pigments have a large influence on the drying properties of the ink. One fact very much in evidence, is that, in general, the more acid the pigment, the longer the drying time. If the drying data of the inks containing no drier is examined, it will be seen that the following pigments do not conform to the above mentioned general rule:

Prussian blue
Titanium dioxide
Monastral blue
Chrome yellow
Hansa yellow
Chrome Green

If this list of pigments is examined it will be noted that prussian blue, chrome yellow, and chrome green are oxidizing pigments that are known to accelerate drying. These pigments, therefore, would not be expected to conform to the above mentioned rule. The abnormal behavior of the other pigments can not as yet be explained.

When drier is added to the printing ink formulations discussed above, the effect of pigment pH is much less noticeable, but the more alkaline pigments are still the more rapid drying. When different drier metals are used, as illustrated in Table VI, no important difference in drying properties is observed. The rule that the more alkaline the pigment, the more rapid the dry, appears to hold also for manganese and lead driers.

It is apparent, however, that additional factors other than pigment pH and oxidizing properties are involved. One of these additional factors is probably pigment particle size.

The conclusions drawn from the results obtained in this work may be stated as follows:

1. Different pigments produce printing inks of widely different drying properties.

2. In general, the greater the pigment pH the shorter the ink drying time.

3. In general, the greater the pigment pH the less the effect of relative humidity on ink drying time.

TABLE IV

INK COMPOSITION

Ink	Pigment	Per cent Pigment	Per cent #3 varnish	Tack at 400 r.p.m. (gram meters)
1	Red Lake C	20	80	25.0
2	Barium Lithol	30	70	23.0
3	Resinated Barium Lithol	20	80	25.2
4	Prussian Blue	30	70	24.6
5	Ultramarine Blue	45	55	25.8
6	Titanium Dioxide	60	40	25.8
7	Monastral Blue	22	78	25.6
8	Chrome Yellow	55	45	24.4
9	Hansa Yellow	30	70	25.1
10	Chrome Green	50	50	25.6
11	Rose Toner	40	60	24.4
12	Malichite green	35	65	24.6
13	Methyl violet	30	70	24.2
14	Cerise Toner	40	60	25.4

TABLE V

EFFECT OF VARIOUS PIGMENTS ON INK DRYING TIME

Data

Each ink made up to a tack of 25 gram meters at 400 R.P.M.
Drier - cobalt naphthenate.
Paper - Duplex Super Varnish

Drying Time in Hrs. At Various Relative Humidities

		40% Relative Humidity Drier conc.				60% Relative Humidity Drier conc.			76% Relative Humidity Drier conc		
Pigment	pH	.0%	.5%	1%	2%	.5%	1%	2%	.5%	1%	2%
Red Lake C	8.9	76.2	5.7	2.7	1.1	6.3	3.9	2.1	7.5	4.4	2.3
Barium Lithol	8.9	79.9	3.5	3.8	2.9	6.6	4.0	2.4	6.1	5.7	2.4
Resinated Barium Lithol	8.5	82.7	4.8	3.5	1.8	6.3	3.9	2.1	7.5	4.4	2.3
Prussian Blue	8.2	29.8	8.7	3.1	3.7	8.7	5.6	3.5	7.9	5.8	3.8
Ultramarine Blue	7.7	114.4	5.5	2.6	*	11.0	3.1	0.8	6.1	2.7	1.3
Titanium Dioxide	7.5	27.2	3.7	1.9	*	9.5	1.8	0.3	14.0	1.6	0.5
Monastral Blue	7.4	168.0	6.3	4.8	4.1	8.8	3.6	4.6	16.0	4.7	3.8
Chrome Yellow	7.2	96.6	8.5	7.9	1.9	7.4	5.6	2.6	13.6	3.8	1.6
Hansa Yellow	6.9	104.0	3.5	2.6	1.6	5.6	3.2	1.9	2.9	4.4	3.0
Chrome Green	5.4	4.7	6.9	3.0	6.1	5.6	3.5	6.0	4.9	3.6	8.1
Rose Toner	5.2	240 +	4.4	2.5	1.5	8.0	3.3	3.1	2.9	4.4	2.4
Malichite Green	5.1	240 +	15.9	7.0	2.2	24 +	7.6	3.4	24 +	7.7	5.1
Methyl Violet Toner	4.6	240 +	24 +	15.5	12.7	24+	18.7	16.3	24 +	24 +	24 +
Cerise Toner	4.3	240 +	20.3	11.0	2.9	24+	16.7	4.3	24 +	24 +	5.5

* Drying Time too short to be recorded.

TABLE VI

EFFECT OF VARIOUS PIGMENTS ON INK DRYING TIME

Data

Each ink made up to a tack of 25 gram meters at 400 r.p.m. 2% Lead and Manganese naphthenate drier (on basis of the varnish) used, containing: 13.1 per cent lead and 2.6 per cent manganese

Pigment	pH	Drying Time in Hours at various Relative Humidities 50% R.H.	62% R.H.	76% R.H.
Red Lake C	8.9	6.6	7.2	8.5
Barium Lithol	8.9	3.0	8.5	9.4
Resinated Barium Lithol	8.5	6.5	8.9	8.8
Prussian Blue	8.2	5.1	5.3	4.6
Titanium Dioxide	7.5	4.6	5.2	2.5
Chrome Yellow	7.2	12.0	10.3	10.3
Hansa Yellow	6.9	12.1	12.2	12.1
Chrome Green	5.4	8.8	7.4	7.0

(Continued on next page)

TABLE VI (continued)

EFFECT OF VARIOUS PIGMENTS ON INK DRYING TIME

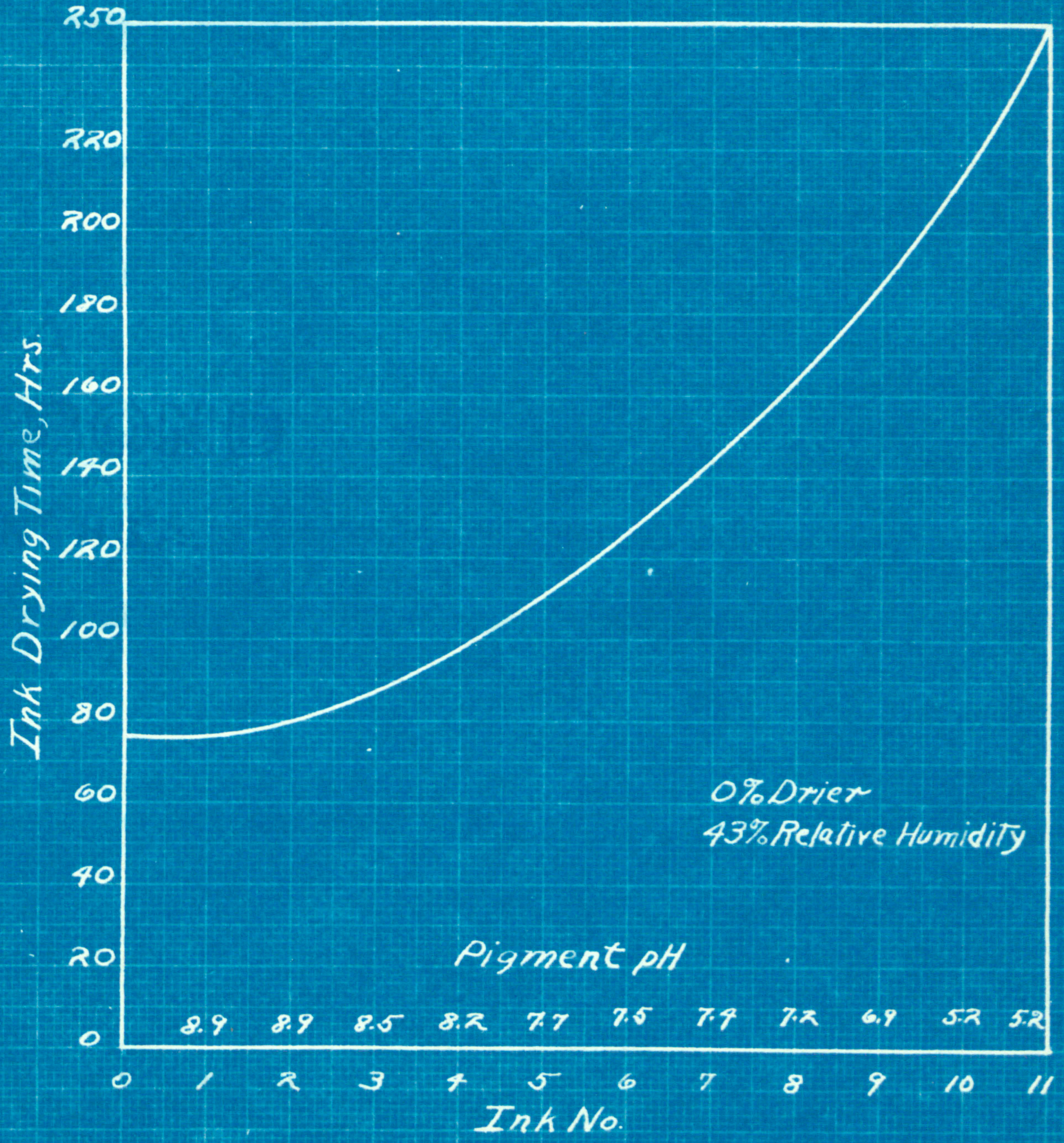
Data

Each ink made up to a tack of 25 gram meters. 1% Lead and manganese naphthenate drier (on basis of ink) used.
Containing: 13.1 per cent Lead
2.6 per cent manganese

Pigment	pH	Drying Time in Hours at various Relative Humidities 43% R.H.	62% R.H.	76% R.H.
Red Lake C	8.9	10.2	14.2	15.2
Barium Lithol	8.9	11.9	10.6	11.3
Resinated Barium Lithol	8.5	9.4	10.8	10.7
Prussian Blue	8.2	6.0	6.6	4.5
Titanium Dioxide	7.5	4.8	6.0	7.2
Chrome Yellow	7.2	11.4	12.7	12.3
Hansa Yellow	6.9	11.0	12.7	12.6
Chrome Green	5.4	—	5.3	4.7

Fig I

EFFECT OF DIFFERENT PIGMENTS ON INK DRYING TIME



3. Effect of Pigment pH on Ink Drying Time

This part of the experimental work consisted in determining, more or less quantitatively, the effect of pigment pH on the drying properties of printing inks. An attempt was made here to prepare or obtain several series of pigments identical in chemical composition and particle size but differing in pH. After repeated trials it was found to be extremely difficult, if not impossible, to make different series of pigments having the above properties. The Binney and Smith Co., however, became interested in this problem and agreed to supply a series of carbon black pigments varying over a range of about two pH units. The chemical composition and particle size of these pigments were as nearly identical as possible.

Five separate inks were made with each of the five carbon black pigments supplied, and their drying times determined at 48, 66, 76, and 92% relative humidity on Champion Duplex Super Varnish paper. These inks were formulated as follows: 30% carbon black pigment, 70% Sinclair & Valentine No. 3 varnish, and 6% cobalt naphthenate drier.

The results of this work are given in Table VII and Fig. II. These results show conclusively that pigment pH is a critical factor controlling the drying properties of printing inks. This fact was strongly suggested by part II of the experimental work, but could not be conclusively stated because other important properties of the pigment could not be held constant. In this part of the work, however, five carbon black pigments of the same particle size and chemical composition, differing only in pH, were studied. The drying rate data obtained indicated conclusively that the greater the alkalinity of the pigment, the more rapid its drying properties. Electron microscope photographs of these pigments (Figures III to VI) are included in this work to substantiate the fact that the pigment particle size of these pigments is constant.

It will be noted in Fig. II that the greater the relative humidity, the more pronounced the effect of pigment pH on drying time. This phenomenon was also noted in part II of the experimental work.

The reason for a decreased drying rate of a printing ink formulated with an acid pigment is probably due to the retarding action that traces of acid have upon the polymerization of drying oils. It has long been known, for example, that rosin will check the increasing body of phenolic or alkyd varnish.

The conclusions which may be drawn from the data obtained in this third part of the experimental work are as follows:

1. Other factors being held constant, the greater the pigment pH, the shorter the ink drying time.

2. The greater the pigment pH, the less the effect of relative humidity on ink drying time.

TABLE VII

EFFECT OF PIGMENT pH ON INK DRYING TIME

Pigment	pH*	pH of sludge	The Drying Time in Hours at various Relative Humidities 48% R.H.	66% R.H.	76% R.H.	92% R.H.
A	2.8	3.1	5.0	6.3	7.7	12.0
B	2.8	2.9	4.2	5.6	7.6	10.1
C	3.8	3.8	3.4	4.5	6.1	7.7
D	4.3	4.2	3.1	3.4	4.6	5.2
E	5.0	4.7	2.8	3.8	4.1	4.7

* pH given by Biney and Smith

Fig II

EFFECT OF PIGMENT pH ON INK DRYING TIME AT VARIOUS RELATIVE HUMIDITIES

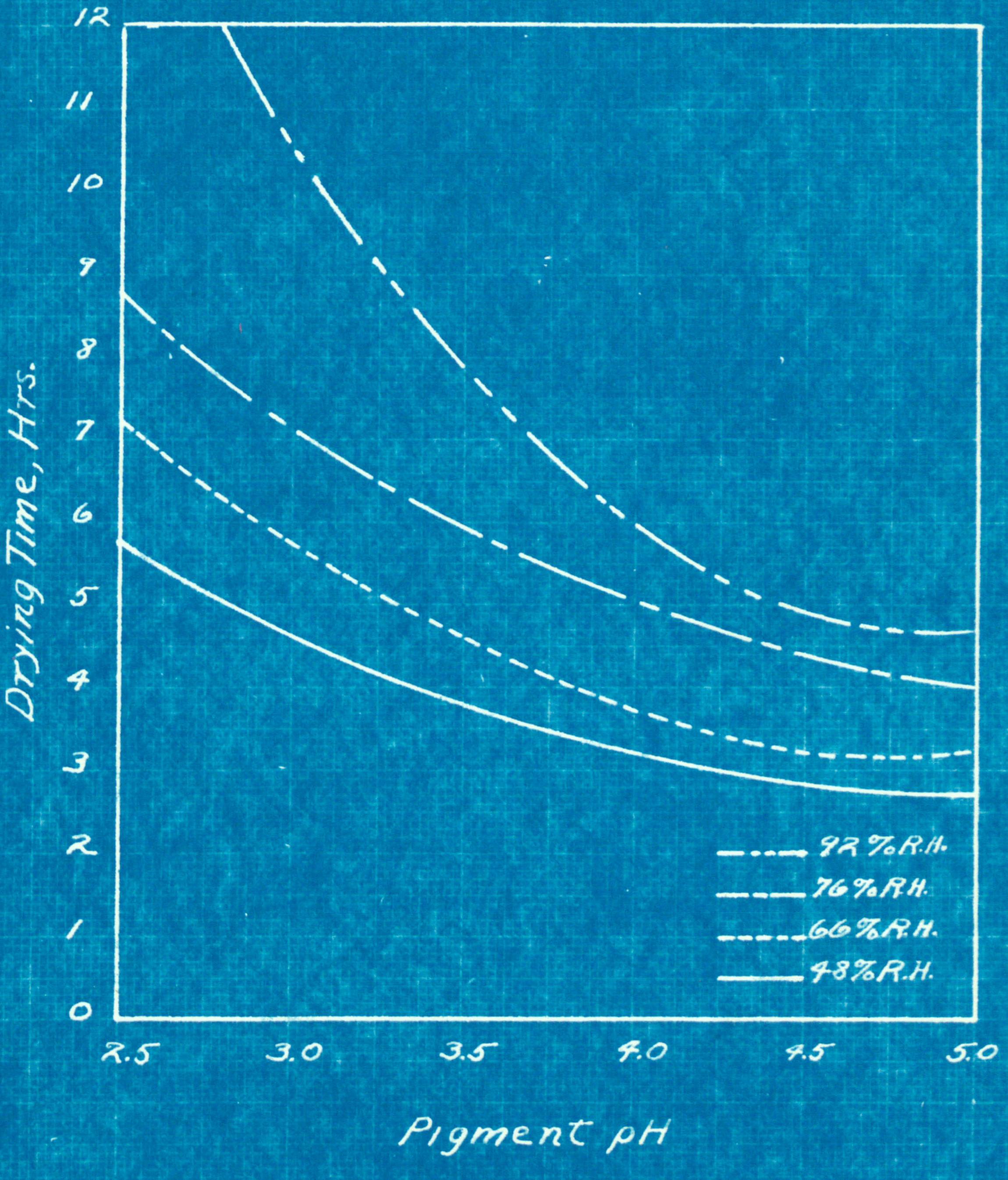
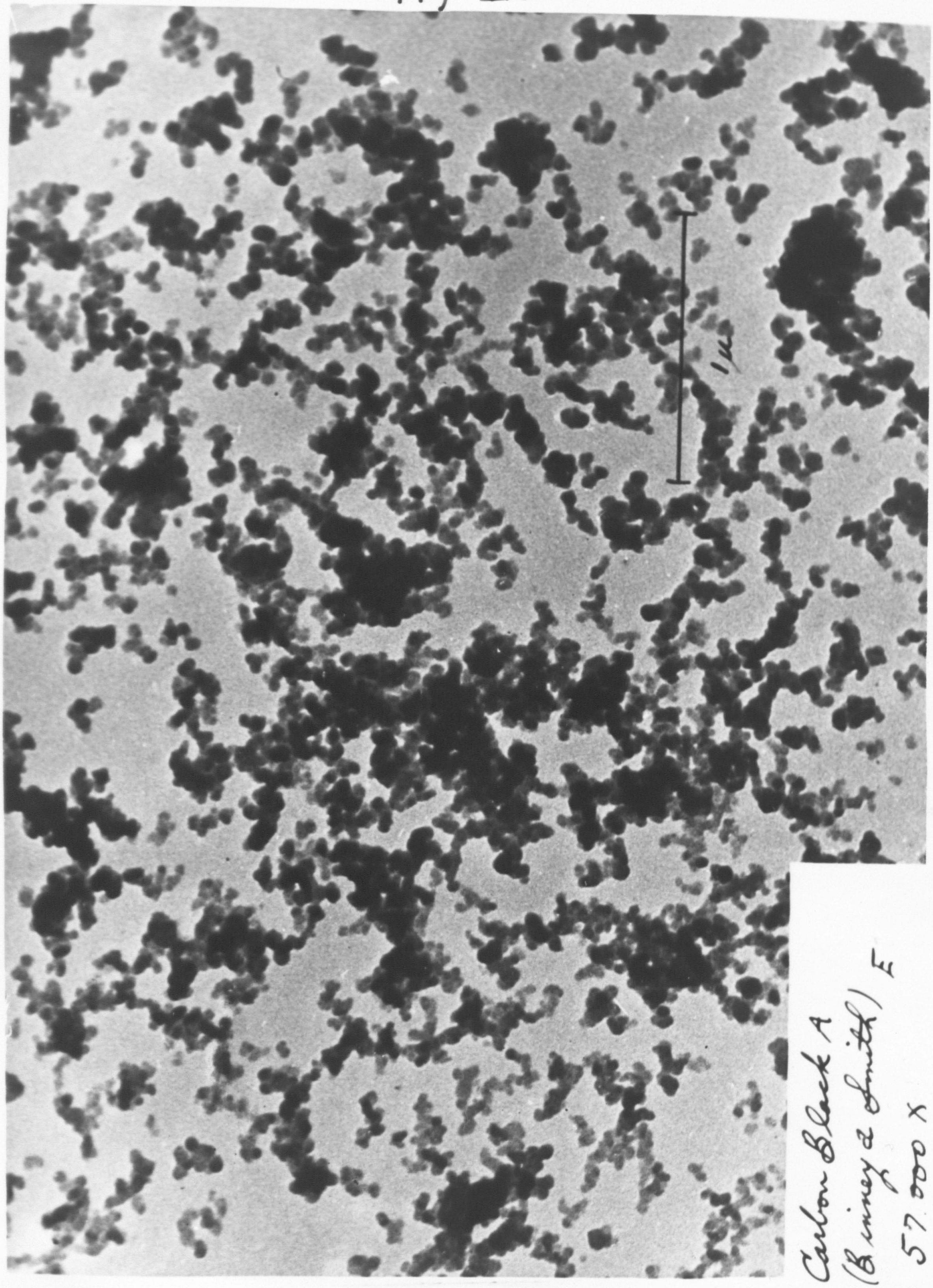
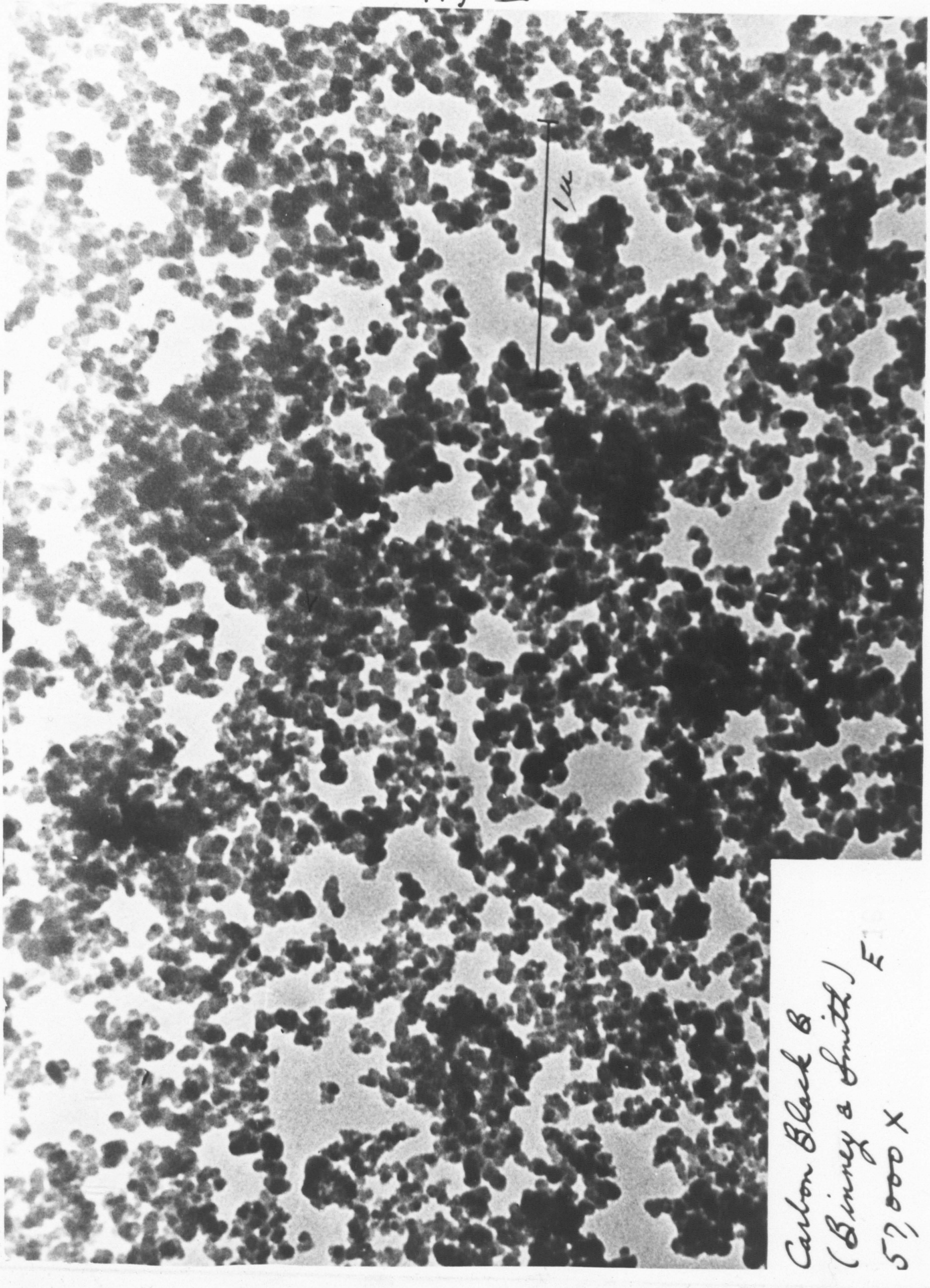


Fig. III



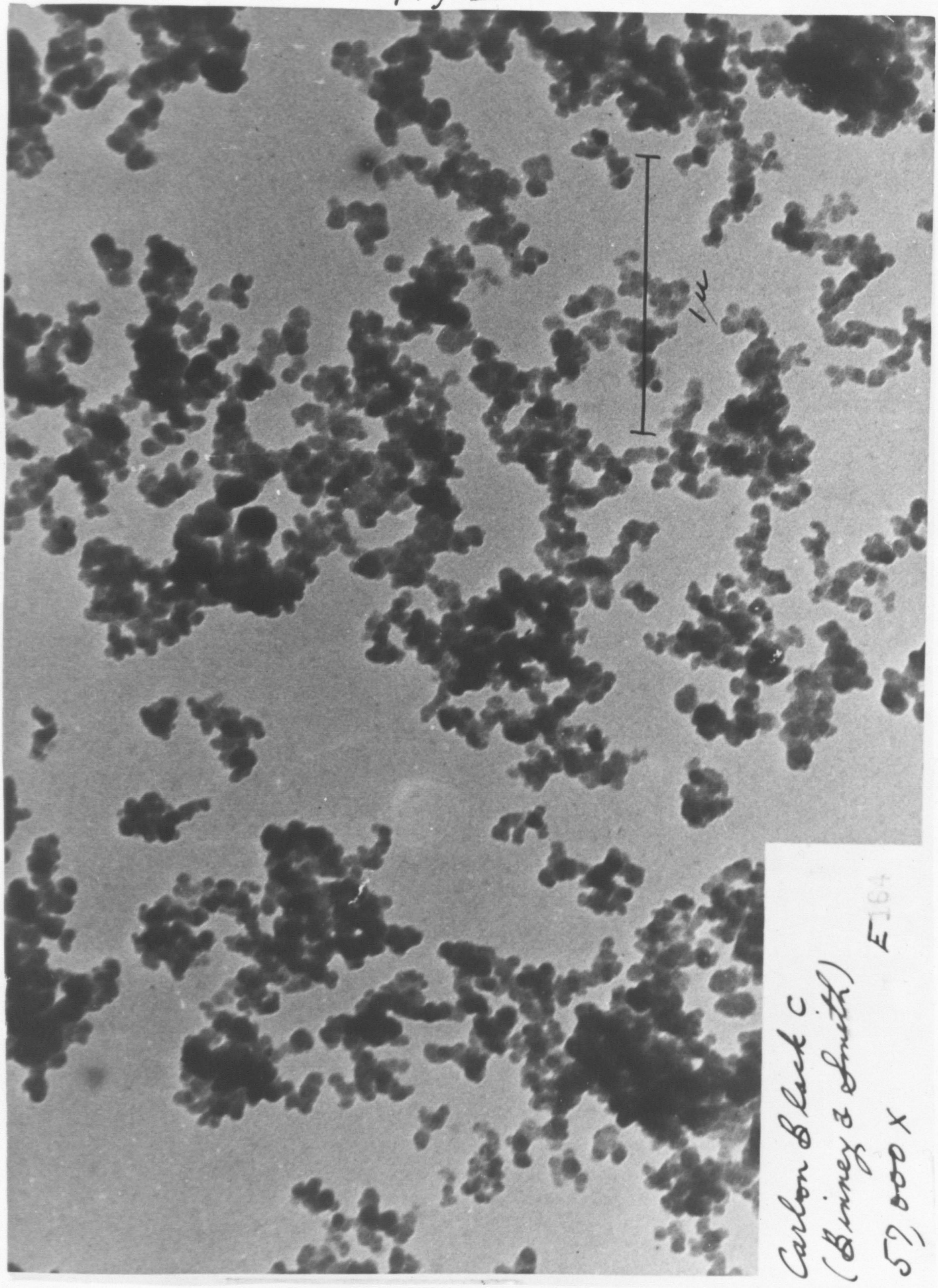
Carbon Black A
(Binney & Smith) E
57,000 X

Fig IV



Carbon Black B
(Binney & Smith)
57,000 X
E

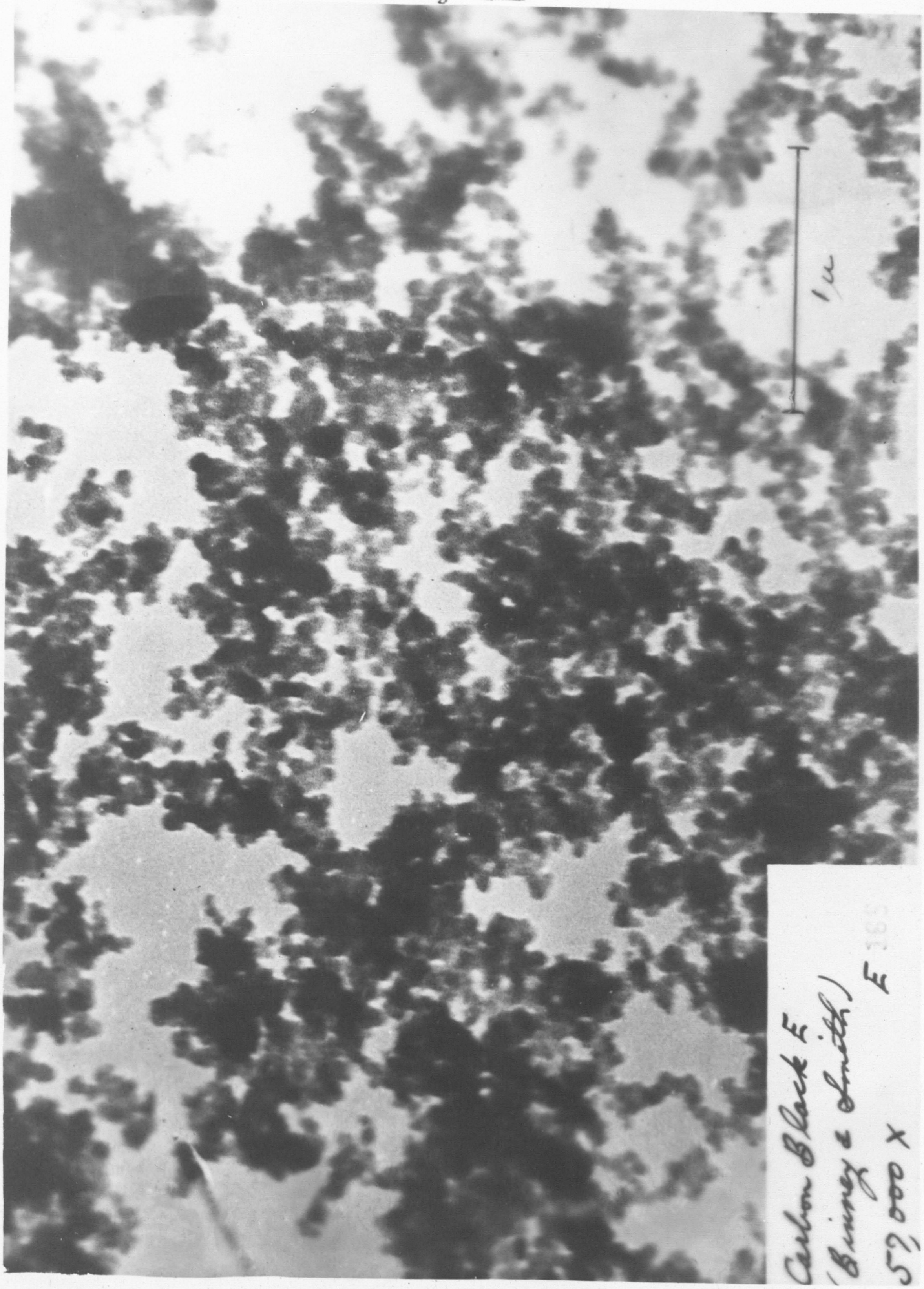
Fig V



Carbon Black C
(Binney & Smith)
57,000 x

E164

Fig VI



4. Determination of Pigment Particle Size and Surface Area

As have been previously mentioned, there are numerous methods of particle size determination. Most of these, however, apply to particles of limited size range and it could not be expected that any one method would prove satisfactory for the fourteen pigments of widely varying particle sizes studied in this work. It was necessary, therefore to critically evaluate the many methods available and to select two or three which would produce reliable results with the relatively simple equipment obtainable.

The first method studied was based on the well proven fact that particles in a non-polar liquid will adsorb upon their surfaces a mono-molecular layer of a polar liquid. A known amount of carefully washed and dried pigment was suspended in a benzene-oleic acid solution of known concentration. The suspension was kept agitated for a period of at least four hours. During this time the adsorption of the oleic acid on the pigment surface was believed complete. The pigment was then sedimented by centrifugal force, and an aliquot portion of the clear supernatant liquid was titrated with a sodium hydroxide solution of known concentration. A glass electrode was used to determine the end point. The difference between the amount of oleic acid present in the original suspension medium and the amount present in the supernatant liquid was equal to the oleic acid adsorbed by the pigment. Knowing the weight of the pigment used, the area of the oleic acid molecule, and assuming the adsorption of a mono-molecular layer, the specific surface could be calculated.

This method was given serious study but the results obtained could not be satisfactorily duplicated. The values in Table VIII are typical of the best data obtained. It can readily be seen that this method was not suitable for accurate work. Therefore, it was abandoned.

The second method studied was a gravitational sedimentation method, utilizing Stoke's Law. The particular procedure used here was developed by W.O. Hinkley.[14] The procedure involved complete dispersion of the pigment in water with the aid of a good mixer. A malted milk mixer or a small colloid mill was recommended. Prolonged mixing with an efficient wetting agent was essential. The suspension was then put into a tall graduated cylinder and allowed to settle. At definite intervals aliquot portions of the suspension were removed at definite depths from the surface. The amount of pigment present in each aliquot portion was determined by the difference between the specific gravity of the aliquot and that of the original suspension. By applying Stoke's Law, the particle size of the pigment settled after each period of time could be calculated. The sample could then be divided into fractions containing pigment particles within a limited size range.

This method has the advantage of being simple and rapid, but suffered the disadvantage of not being applicable to pigments of small particle size. Pigments having a particle size of less than 0.5 microns could not be broken down to their individual particles even by violent prolonged agitation. Also the time required to sediment finely divided particles proved far too long for practical purposes.

This method was abandoned in favor of a centrifugal sedimentation method. There are numerous centrifugal sedimentation methods mentioned in the literature. The one used here, however, was developed by S. W. Martin[15] especially for the particle size determination of pigments.

In this method a varnish was selected which had good wetting properties for the pigments whose particle sizes were to be determined. A paste consisting of 50% varnish and 50% pigment by weight was made and ground twice over a small laboratory mill with the rollers set for a tight grind. The paste was then dissolved in sufficient V.M.&P. naphtha to produce a suspension of either 2 or 5% total solids depending upon the specific gravity of the pigment.used. A second solution was then made containing only varnish and naphtha in exactly the same amounts as the suspension described above. This solution was the sedimentation medium and its coefficient of viscosity was accurately determined at the temperature of the sedimentation. An Ostwald viscometer was used to determine this viscosity.

Four aliquot portions of a pigment suspension were placed in four balanced centrifuge tubes and centrifuged for a definite time at a definite r.p.m.. The four tubes were then removed and an aliquot portion of the supernatant liquid removed by means of a pipette lowered to within one quarter inch of the surface of the sedimented pigment cake. The specific gravity of this liquid was then determined. This process was repeated with progressively increasing centrifuging times until from five to ten aliquots were centrifuged. The last aliquot of suspension was centrifuged for a sufficiently long time to have sedimented almost all of the pigment present. The amount of pigment sedimented was then calculated from the difference between the specific gravity of the original suspension and that of the final suspension.

From the weights of pigment sedimented after each interval of time, a sedimentation curve may be drawn with per cent of sedimented pigment as ordinate and time as abscissa.

In order to construct a scale in microns corresponding to sedimentation times, the following formula may be used:

$$D - \frac{6}{W}\sqrt{\frac{n \ln R/S}{2\,(d_1 - d_0}})t \quad \text{where}$$

D = the equivalent diameter in centimeters of the particle of average weight,

$W = 2N/60$ where N is the number of revolutions per minute,

n = coefficient of viscosity of the medium,

R = distance from the axis of rotation to the bottom of the centrifuge tube,

S = distance from the axis of rotation to the meniscus of the suspension,

d_1 and d_0 = specific gravity of the pigment and of the suspension respectively, and

t = time of centrifuging in hours.

Once the particle size distribution curve has been determined it is possible to find: (1) the surface area per gram, (2) the surface area per cc of pigment, and (3) the average particle diameter from[16] the following formulas:

1. Surface area in square centimeters per gram -

   $S = \frac{K \times 10^2}{D_s} \sum (G_f/d_f)$ where

   D_s = density of pigment,

   G_f = weight percentage in each fraction for which d_f is mean size in microns, and

   K = shape constant ratio (equal to 6 for spheres).

2. Surface area per cc -

   surface area per gram times specific gravity
   equals Surface area per cc.

3. Average particle diameter (surface mean diameter, D^1)

   $D^1 = \frac{K \times 10^4}{S \times D_s}$ where

   K = shape constant ratio

   S = surface area in square centimeters per gram, and

   D_s = specific gravity of the pigment.

The percentage by weight of the pigment falling between definite particle size limits, can be conveniently determined by drawing tangents to the sedimentation curve at the desired limits. The length of the ordinate, between the intersection of the two tangents is numerically equal to the per cent by weight of the pigment falling within the particle size interval. The method was developed by Oden and is completely described in reference No. 22.

Centrifuge data for this method is given in Table IX. The results of this work are given in Tables X to XVIII and Figures VII to XV.

In addition to the sedimentation methods utilizing Stoke's Law, a number of methods, called adsorption methods, have been developed using the principle of mono-molecular adsorption advanced by Irving Langmuir.

The first practical adsorption method was developed by Emmett and his co-workers.[17] This method is based upon the mono-molecular adsorption of nitrogen gas on the pigment surface at a very low temperature. A complete description of this method is given in numerous articles.

This method has been improved and used with great success by numerous investigators. It is considered to be one of the better methods of determining pigment particle size. It has, however, the serious drawback of requiring elaborate and expensive apparatus, and also a very low operating temperature. For these reasons this method could not be used in this work.

A much simpler method based upon the same principle was developed by D. Smith and H. Green.[18] The procedure of this method was to expose a weighed amount of perfectly dry pigment to an atmosphere containing a rather large amount of water vapor in a completely closed system. The resulting loss of pressure was accurately measured with an inclined manometer, and since the magnitude of the pressure loss is proportional to the surface area of the exposed pigment, the specific surface and the particle size of the pigment could readily be calculated.

Considerable time and effort were spent studying this method. At the outset it showed promise, but after the apparatus was built and tried, many difficulties arose which made it extremely difficult to obtain reliable data. The entire system had to be absolutely air tight. The decrease in pressure caused by the adsorption of water vapor by the pigment sample was in most cases so minute that the smallest leak would completely ruin the results. The handling of the appartus that was necessary to insert pigment samples would continually introduce new leaks. Rubber tubing could not be used. In addition, almost the entire appartus had to be submerged in a constant temperature water bath. This further increased the difficulty of manipulating the apparatus. Because of these difficulties, this method was finally abandoned.

Carbon black pigments, however, because of their tremendous surface area, caused a much larger decrease in pressure upon adsorption of water vapor than did other pigments. This fact tended to nullify the effect of slight leakage and fair results were obtained. Examples of these results are given in Tables XIX and XX.

The data obtained for Peerless Black are in the correct range and reproducible with a fair degree of accuracy. The results obtained with Super Carbovar, although reproducable with good accuracy, do not agree with values obtained by the Emmet and DeWitt adsorption method.

The remaining methods investigated were visual examination with the ordinary microscope and also examination with the electron microscope. Examination with the ordinary microscope is direct and simple and furnishes a reliable check on the other methods used. It should be pointed out, however, that only pigments of particle size greater than 0.2 microns are visible under the ordinary microscope. The value obtained for pigments of greater particle size than 0.25 microns were considered to be fairly accurate since a diameter greater than 0.25 microns is well within the range of the visual microscope.

The microscopic method used here was an adaptation of that of Green.[19] The pigment to be examined was ground in sufficient No. 3 varnish to produce an ink with a tack of 25 gram meters ase measured with the Inkometer. Two passes over a three roller laboratory mill were considered sufficient for good distribution of the pigment. A small portion of this ink was dispersed in a solution of one part of butyl acetate and two parts of petroleum ether. A drop or two of this suspension was put on a microscope slide and rubbed into a very thin film with a glass rod. The film dried rapidly and the pigment particles adhered well enough so as to eliminate the need of a cover slip. A drop of cedar oil was placed on the slide and it was then photographed under the oil immersion lense according to standard methods. The results of this work are given in Table XXI.

The best method of determining pigment particle size is unquestionably examination under the electron microscope. The range of magnification is almost unlimited; pigments of any size, however small, can readily be examined. Also the nature of the pigment surface, which before the advent of the electron microscope could not be determined, is now easily examined.

An electron microscope was used in this work to obtain a better value of pigment particle size, surface area, and pigment surface condition. The laboratory in which this work was done did not have an electron microscope. This thesis, however, was completed at the Naval Research Laboratory where an electron microscope was available.

The technique of mounting the pigment samples for examination with the electron microscope has been developed largely by Wiegand of the Columbian Carbon Company. Of the three methods of mounting pigments for electron microscope examination commonly used, the method employed in this work involved the suspension of the pigment particles on $\frac{1}{4}$ inch discs of very fine wire mesh. A complete description of this method of mounting is given in reference 20. The results of this work are given in Figures XVI to XXVII.

In discussing the results obtained in this part of the experimental work each of the three methods of particle size determination finally used will be examined. It was not intended that any one method would supply reliable particle size data of all the pigments studied. For this reason three methods of different principle were used. It should also be emphasized that no great effort was put on any one method with the idea of accepting its values as final. An average value of three absolutely independent methods was considered more reliable.

The centrifugal sedimentation method used in this work had the important advantage of determining the pigment particle size after it had been ground into the ink. Roller mill grinding does not necessarilly reduce the pigment to its individual particle size, but it does reduce the pigment agglomerates to the size they possess in the practical, finished ink. In some instances, however, where the pigment particle size is 3 microns or larger, a "tight" roller mill grind could possibly further reduce the particle size.

One of the disadvantages of this method is its limitation to pigments whose particle sizes were greater than 0.1 micron. Excellent agreement is reported down to 0.1 micron; beyond this size the accuracy of the method falls off rapidly. Svedberg and Nichols, however, have obtained good agreement down to particle sizes of the order of 20 milli-microns with the ultracentrafuge.[21] With ordinary apparatus, however the lower limit of particle size is generally set at 0.1 micron. Another serious difficulty with this method which greatly limited its use was the absolute necessity of a vehicle that would thoroughly wet the particular pigment in question and, when diluted with a suitable solvent, would keep the pigment from flocculating. Other workers, whose intent had been to determine with great accuracy the particle size distribution of one particular pigment, studied numerous vehicles, vehicle additives, and solvents, the combination of which would satisfy these requirements. In this work, however, where particle size data was required of fourteen different pigments, a simpler method was devised.

The vehicle used in this work would satisfactorilly wet all of the pigments studied and would keep the great majority of them from flocculating upon dilution. The following pigments flocculated upon dilution and particle size distribution data could not be obtained for them:

Hansa yellow
Malachite green
Titanium dioxide
Prussian blue
Red lake C.

The visual microscope method proved excellent for pigments of particle size greater than 0.25 micron. Particle diameters smaller than this were beyond the range of the oil immersion objective. The chief disadvantage of this method was the very small field for examination. This disadvantage could be overcome at least in part, however, by examination of a large number of fields.

Particle size determination by the use of the electron microscope proved to be the most versatile method. Its resolving power was more than adequate for the smallest pigments studied.

The electron microscope has some disadvantages, however. Pigments that tend to fuse at moderately high temperatures cannot be examined with accuracy. The electron bombardment to which the object is subjected developes a considerable amount of heat. The rather blurred photomicrograph of resinated barium lithol is an example of this type of pigment.

It is extremely important to eliminate pigments which are slightly volatile or produce volatile products when heated. If volatile substances are present, they will partially destroy the high vacuum necessary and, therefore, impede the flow of electrons. This produces distorted, unsatisfactory photomicrographs.

The results obtained by these three methods are tabulted in Table XXI. The results indicate a rather good overall agreement. There are some interesting phenomena brought to light by these comparisons.

The values obtained for the particle size of barium lithol are interesting. The electron microscope photomicrograph pictures a rather large particle approximately 3 microns long and one micron wide. Both the sedimentation method and the visual microscope method indicate a much smaller particle. It should be remembered, however, that both the sedimentation and visual microscope methods utilized a ground paste of the pigment, whereas, the electron microscope utilized the dry powder. This fact suggests that the pigment particle size was materially reduced by grinding. This action might be expected since the particle size of barium lithol is unusually large.

The large value of monastral blue obtained by the sedimentation method is probably due to the remarkable tendency of this pigment to agglomerate. Monastral blue has long been known as a very difficult pigment to grind. It becomes very"buttery" and has no length. The value, 0.99 micron is undoubtedly the diameter of the agglomerate.

The large value obtained for rose toner by the sedimentation method can readily be seen to be in error when the electron microscope photomicrograph is examined. The pigment appears to be highly agglomerated, which strongly suggests that this value represents the size of the agglomerate and not the size of the individual pigment particle.

TABLE VIII

SPECIFIC SURFACE OF CHROME YELLOW PIGMENT

Liquid Adsorption Method

Sample No.	Specific Surface (m^2/g)
1.	2.54
2.	2.54
3.	6.55
4.	1.27

TABLE IX

CENTRIFUGAL SEDIMENTATION DATA

Specific Gravity of Pigments Tested

Barium Lithol	1.67
Resinated Barium Lithol	1.64
Ultramarine Blue	2.37
Monastral Blue	1.48
Chrome Yellow	6.88
Chrome Green	3.43
Rose Toner	2.46
Methyl Violet Toner	1.94
Cerise Toner	2.46

Varnish Used

Sinclair & Valentine 0000 Varnish

Paste Composition; Per Cent by Weight

50% Pigment
50% Varnish

Dilution Medium

Varnish Makers and Painters Naphtha

Centrifuge Data

Distance from the axis of rotation to the bottom of the centrifuge tube - (R) - 19.5cm.

Distance from the axis of rotation to the meniscus of the suspension - (S) - 9.5cm.

1800 r.p.m.

Per Cent Total Solids of Suspension

2% total solids
5% total solids for chrome yellow and chrome green

Coefficient of Viscosity of Suspension Medium - .007579 poise at 28° C.

TABLE X

PARTICLE SIZE DISTRIBUTION DATA FOR BARIUM LITHOL

Per Cent Pigment Sedimented per Unit Time

Time of Centrifuging in Minutes	Per Cent Sedimented
1	44.9
3	80.5
6	100.0
15	100.0
40	100.0

Particle Size Distribution

Diameter in microns	Per Cent Total Pigment
> 2	0
2.0 - 1.5	34
1.5 - 1.0	32
1.0 - 0.92	6
0.92- 0.0	27

Average Diameter = 0.94 microns

Surface Area per gram = 3.79 square meters

Surface Area per cc = 6.33 square meters

Fig VII

Particle Size Distribution Curve
For
Barium Lithol

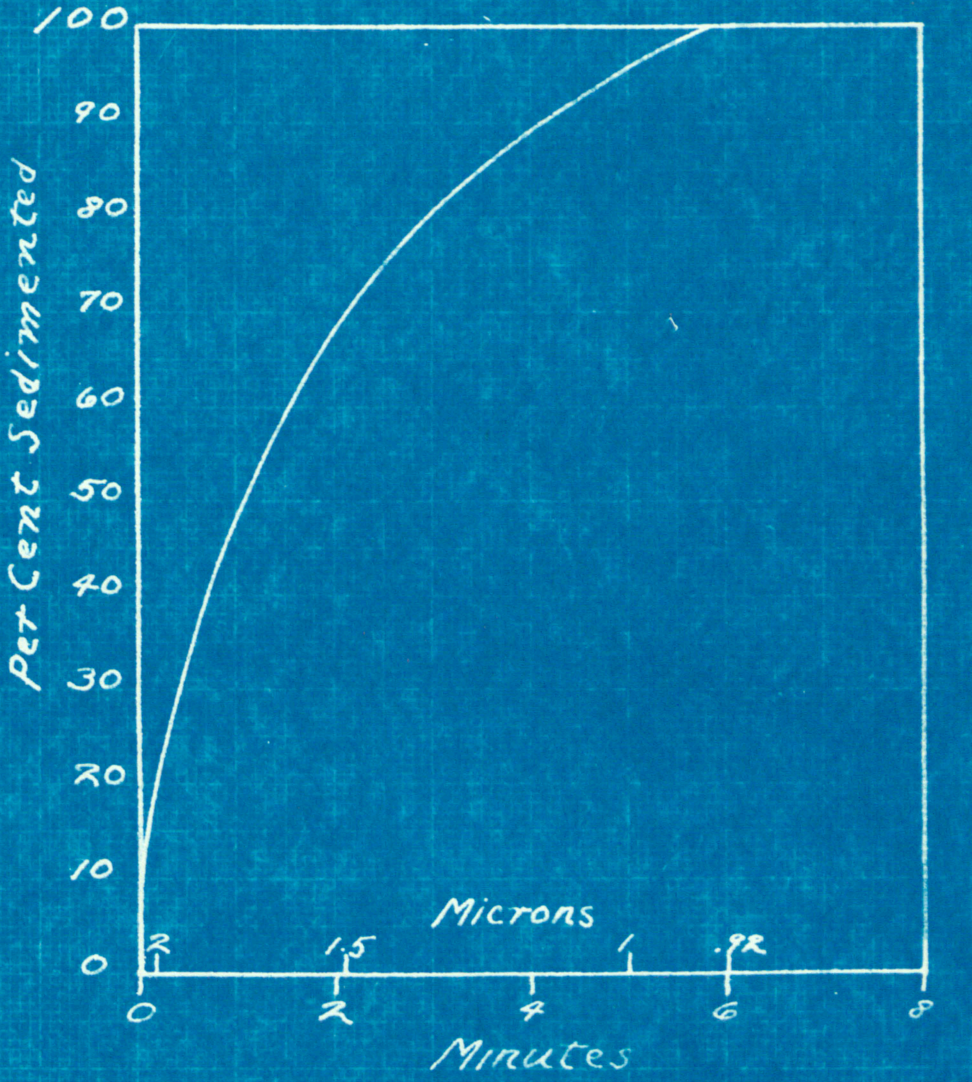


TABLE XI

PARTICLE SIZE DISTRIBUTION DATA FOR RESINATED BARIUM LITHOL

Per Cent Pigment Sedimented per Unit Time

Time of Centrifuging in Minutes	Per Cent Sedimented
1	5.4
3	13.9
6	17.2
15	25.4
33	32.0

Particle Size Distribution

Diameter in microns	Per Cent Total Pigment
> 2	2
2.0 - 1.0	7
1.0 - 0.5	11
6.5 - 0.4	6
0.4 - 0.36	7
0.36 - 0.0	67

Average Diameter = 0.26 microns

Surface Area per Gram = 14.16 square meters

Surface Area per cc = 23.2 square meters

Fig VIII

Particle Size Distribution Curve
For
Resinated Barium Lithol

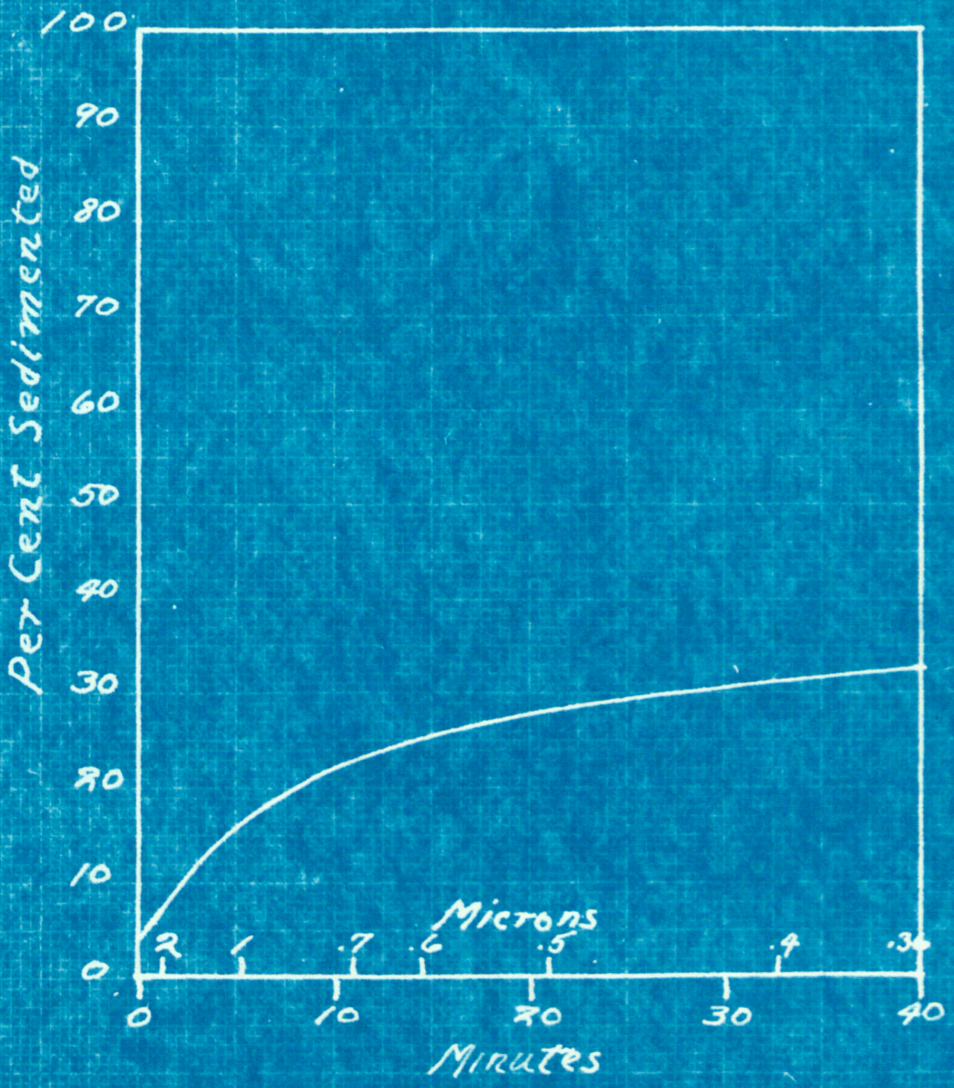


TABLE XII

PARTICLE SIZE DISTRIBUTION DATA FOR ULTRAMARINE BLUE

Per Cent Pigment Sedimented per Unit Time

Time of Centrifuging in Minutes	Per Cent Sedimented
1	6.7
3	25.2
6	46.5
15	56.1
30	56.6

Particle Size Distribution

Diameter in microns	Per Cent Total Pigment
> 1	0
1.0 - 0.5	48
0.5 - 0.4	7
0.4 - 0.3	0
0.3 - 0.27	0
0.27- 0.0	43

Average Particle Size = 0.25 microns

Surface Area per gram = 9.78 square meters

Surface Area per cc = 23.5 square meters

Fig IX

Particle Size Distribution Curve
For
Ultramarine Blue

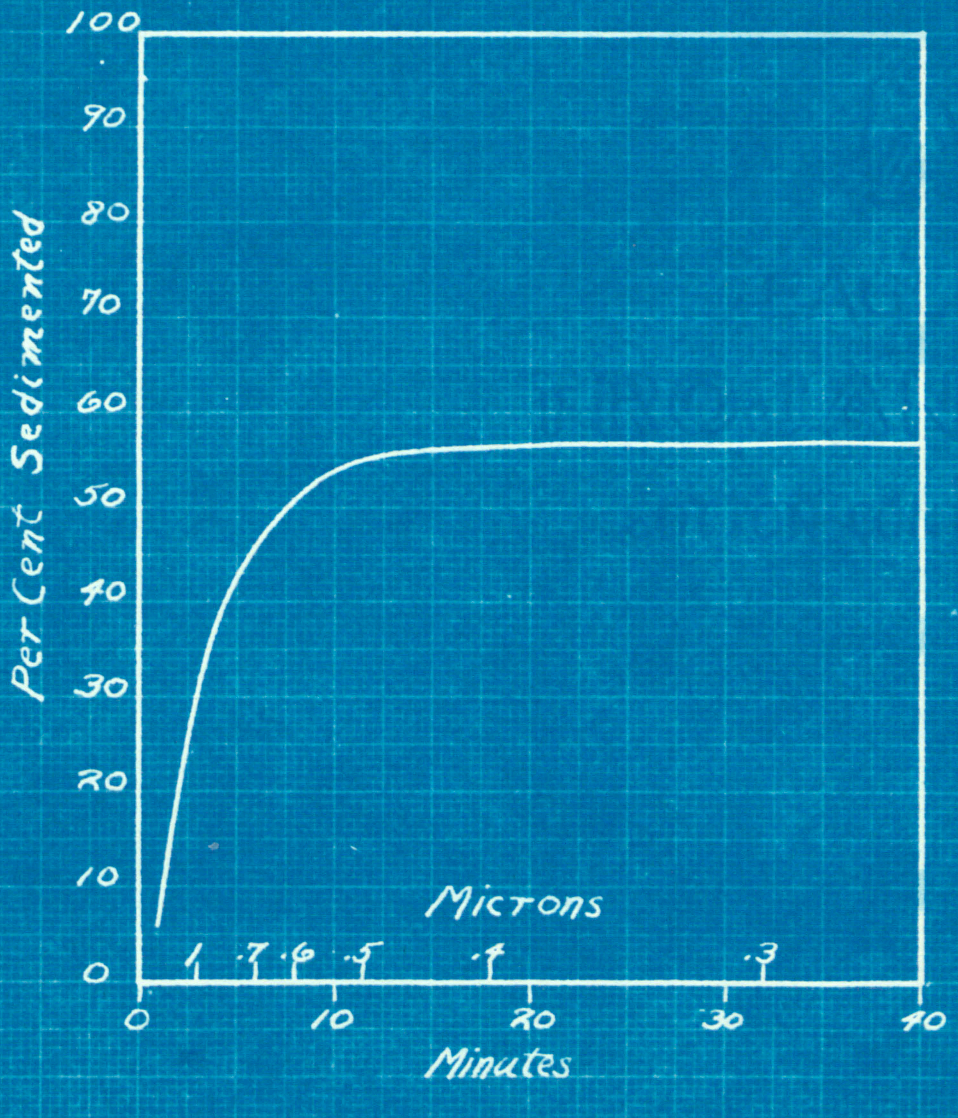


TABLE XIII

PARTICLE SIZE DISTRIBUTION DATA FOR MONASTRAL BLUE

Per Cent Pigment Sedimented per Unit Time

Time of Centrifuging in Minutes	Per Cent Sedimented
1	59.6
3	91.7
15	95.1
40	96.4

Particle Size Distribution

Diameter in microns	Per Cent Total Pigment
> 2	45
2.0 - 1.0	48
1.0 - 0.5	4
0.5 - 0.0	3

Average Diameter = 0.99 microns

Surface Area per gram = 2.73 square meters

Surface Area per cc = 4.04 square meters

Fig X

Particle Size Distribution Curve
for
Monastral Blue

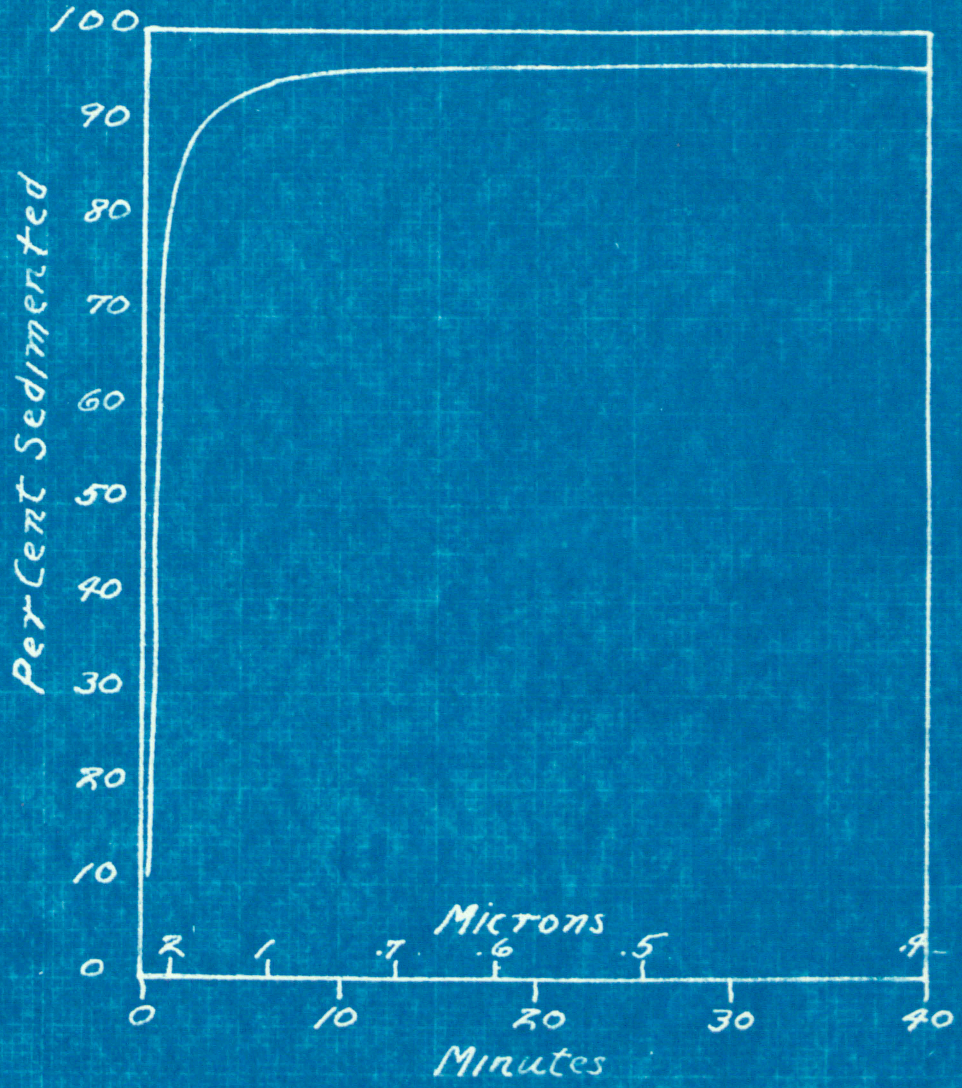


TABLE XIV

PARTICLE SIZE DISTRIBUTION DATA FOR CHROME YELLOW

Per Cent Pigment Sedimented per Unit Time

Time of Centrifuging in Minutes	Per Cent Sedimented
0.68	6.77
2.8	28.25
4.4	66.4
7.7	80.0
17.4	84.8
30.3	84.8

Particle Size Distribution

Diameter in microns	Per Cent Total Pigment
> 1	0
1.0 - 0.5	34
0.5 - 0.4	13
0.4 - 0.3	16
0.3 - 0.2	20
0.2 - 0.15	2
0.15- 0.0	15

Average Diameter = 0.25 microns

Surface Area per gram = 3.5 square meters

Surface Area per cc = 24.0 square meters

Fig XI

Particle Size Distribution Curve
for
Chrome Yellow

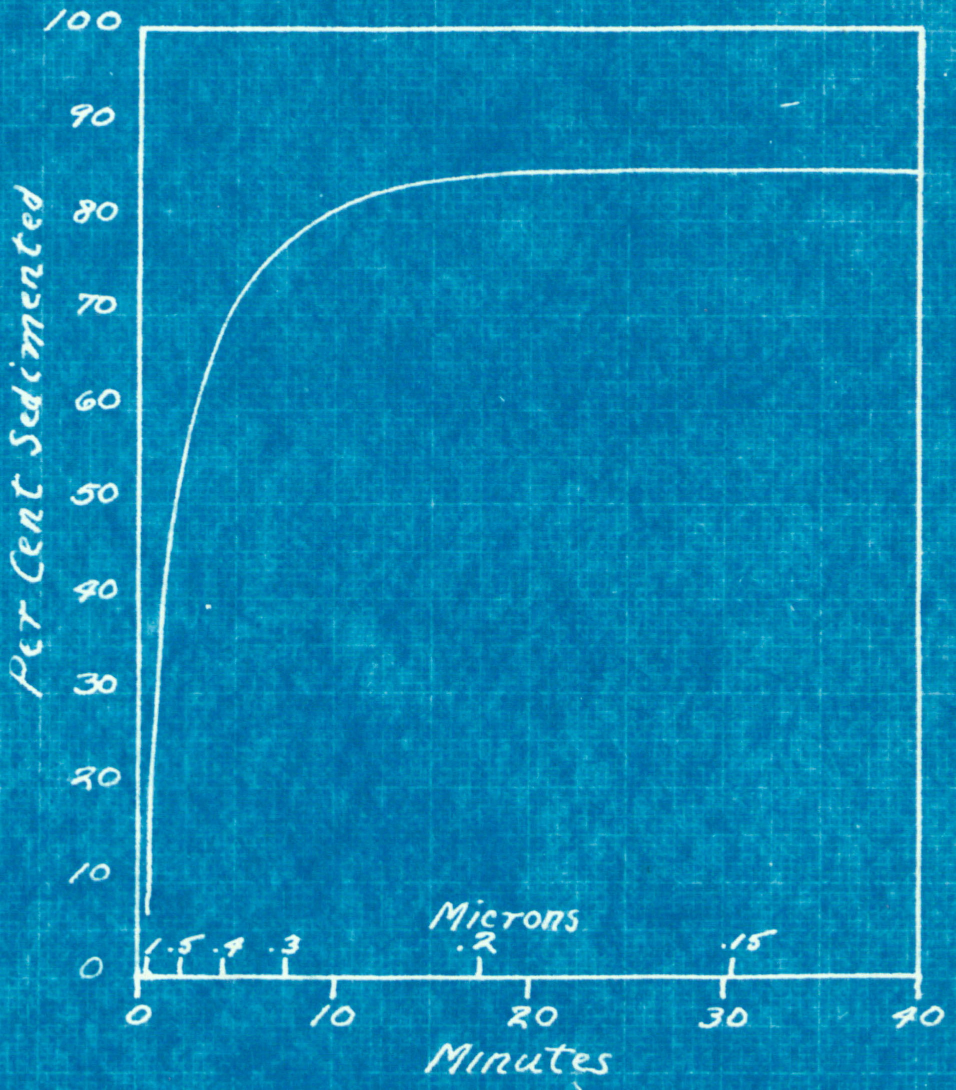


TABLE XV

PARTICLE SIZE DISTRIBUTION DATA FOR CHROME GREEN

Per Cent Pigment Sedimented per Unit Time

Time of Centrifuging in Minutes	Per Cent Sedimented
1	8.3
3	11.5
6	25.0
15	33.0
30	37.0

Particle Size Distribution

Diameter in microns	Per Cent Total Pigment
> 2	2
2.0 - 1.0	15
1.0 - 0.5	10
0.5 - 0.4	3
0.4 - 0.3	6
0.3 - 0.0	62

Average Diameter = 0.10 microns

Surface Area per gram = 16.8 square meters

Surface Area per cc = 57.1 square meters

Fig XII

Particle Size Distribution Curve
For
Chrome Green

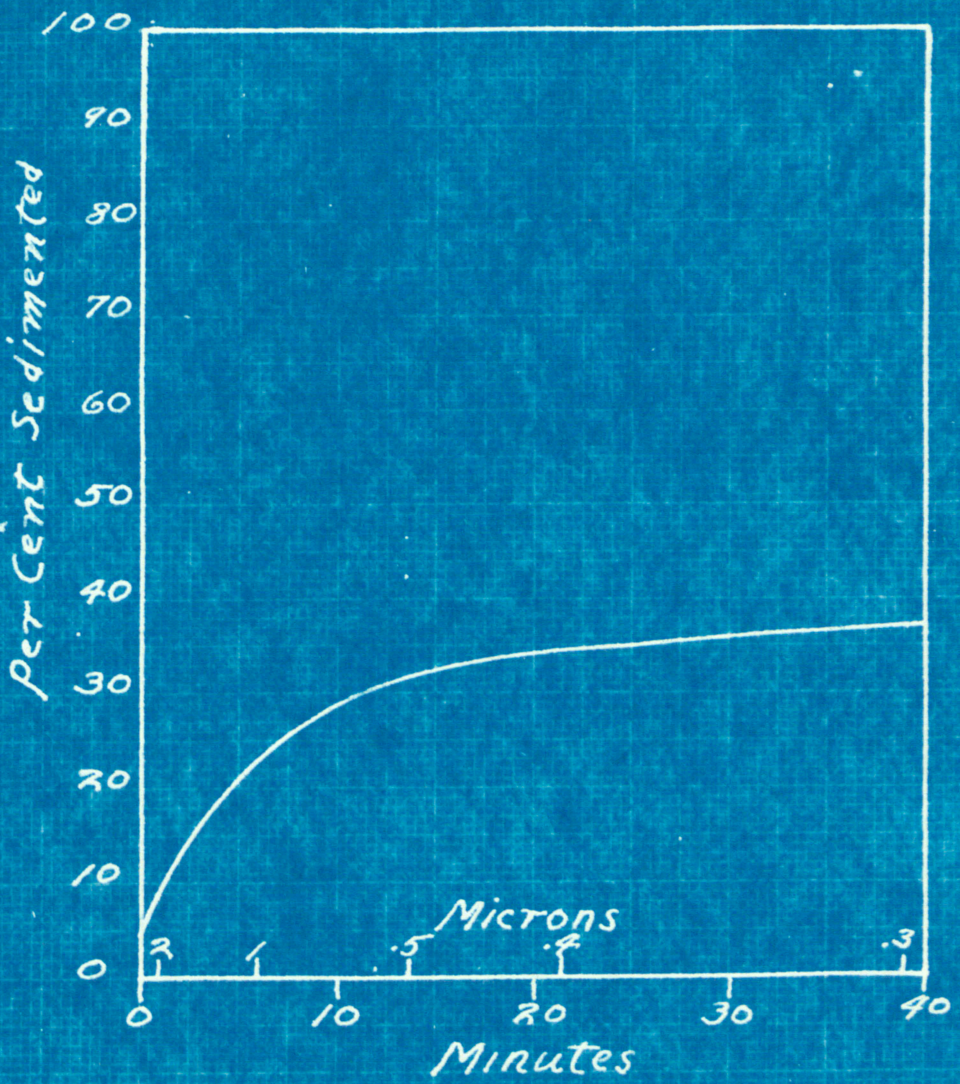


TABLE XVI

PARTICLE SIZE DISTRIBUTION DATA FOR ROSE TONER

Per Cent Pigment Sedimented per Unit Time

Time of Centrifuging in Minutes	Per Cent Sedimented
2.7	20.6
3.0	50.6
6.0	70.3
8.0	89.9
17.0	95.6
30.2	95.6

Particle Size Distribution

Diameter in microns	Per Cent Total Pigment
> 1	0
1.0 - 0.5	70
0.5 - 0.4	18
0.4 - 0.3	8
0.3 - 0.0	4

Average Diameter = 0.55 microns

Surface Area per gram = 4.45 square meters

Surface Area per cc = 11.1 square meters

Fig XIII

Particle Size Distribution Curve For Rose Toner

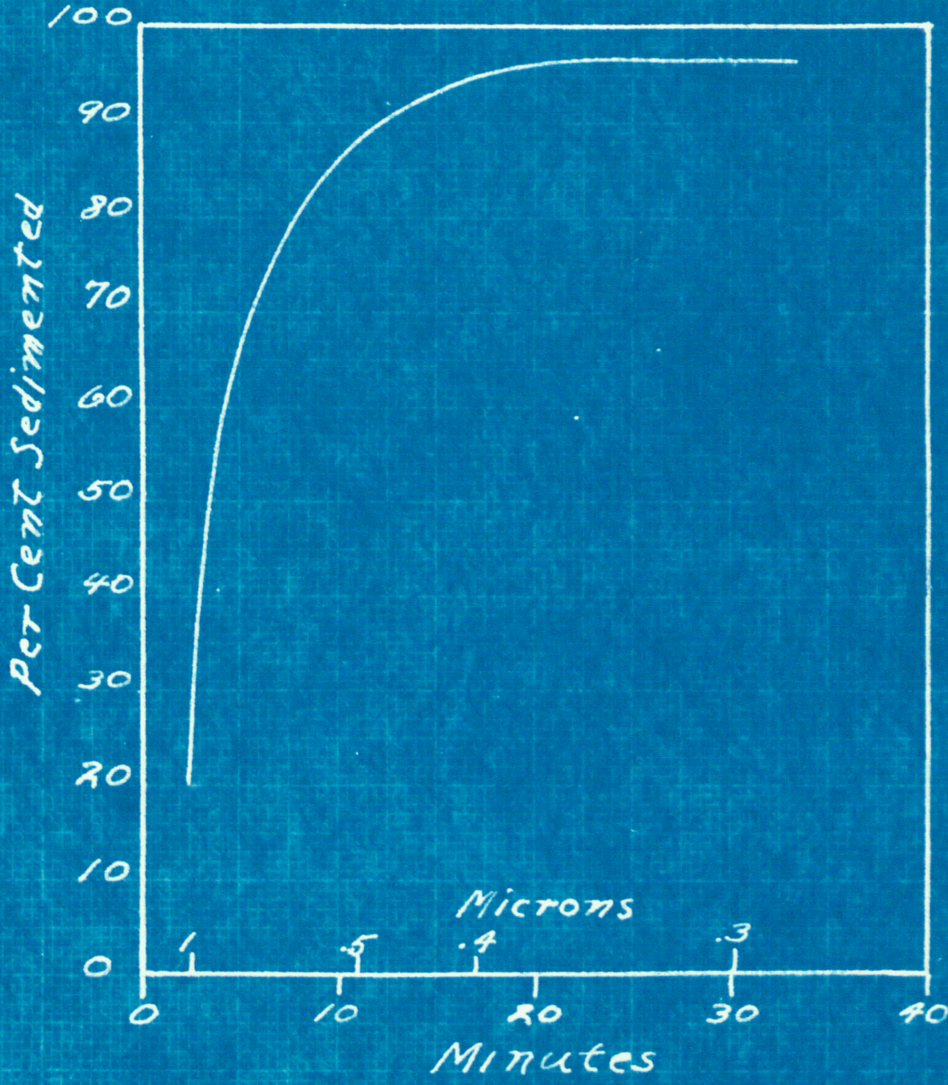


TABLE XVII

PARTICLE SIZE DISTRIBUTION DATA FOR METHYL VIOLET TONER

Per Cent Pigment Sedimented per Unit Time

Time of Centrifuging in Minutes	Per Cent Sedimented
1	20.4
3	27.4
6	41.3
15	52.1
30	66.4

Particle Size Distribution

Diameter in microns	Per Cent Total Pigment
> 1	14
1.0 - 0.5	16
0.5 - 0.4	4
0.4 - 0.3	9
0.3 - 0.24	14
0.24 - 0.0	43

Average Diameter = 0.28 microns

Surface Area per gram = 10.87 square meters

Surface Area per cc = 21.1 square meters

Fig XIV

Particle Size Distribution Curve
for
Methyl Violet Toner

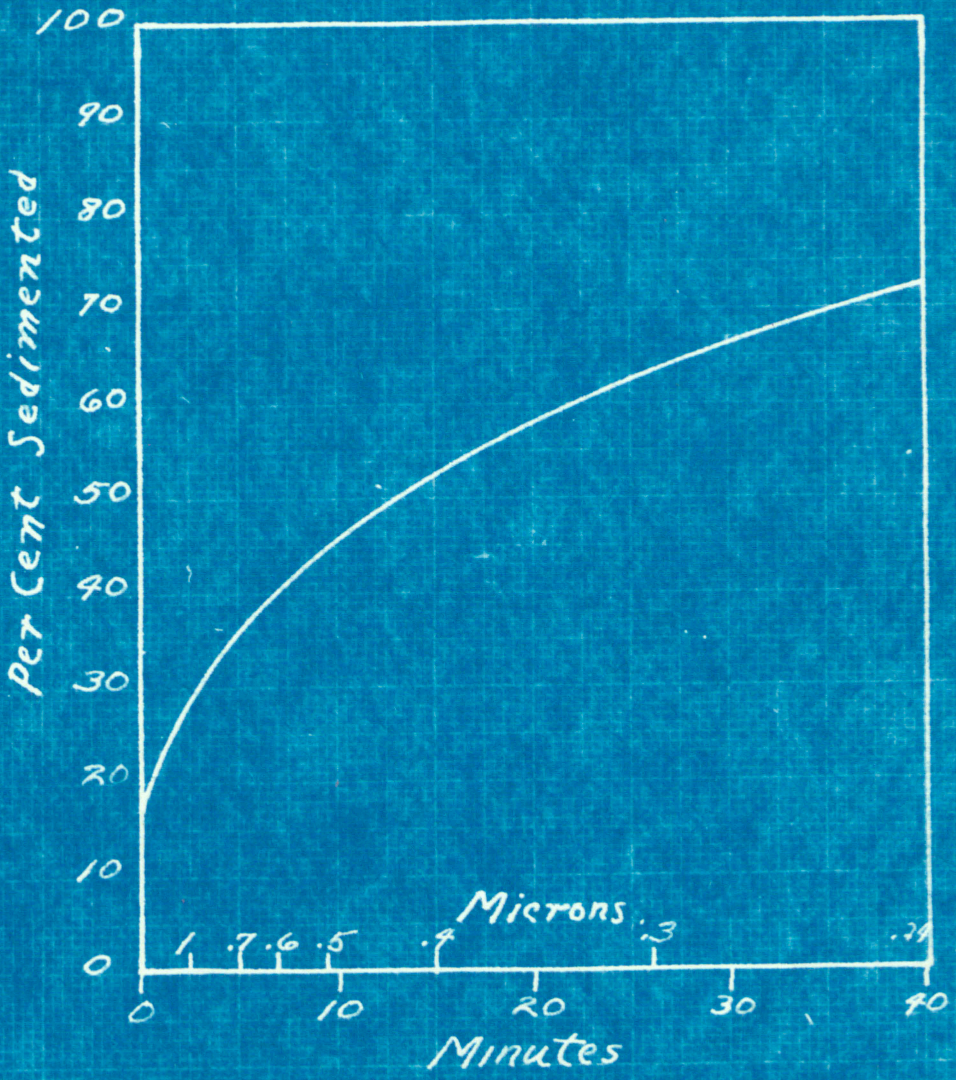


TABLE XVIII

PARTICLE SIZE DISTRIBUTION DATA FOR CERISE TONER

Per Cent Pigment Sedimented per Unit Time

Time of Centrifuging in Minutes	Per Cent Sedimented
2.7	12.2
4.0	36.5
6.0	49.7
17.0	77.8
30.2	91.8

Particle Size Distribution

Diameter in microns	Per Cent Total Pigment
> 1	0
1.0 - 0.5	46
0.5 - 0.4	13
0.4 - 0.3	33
0.3 - 0.0	8

Average Diameter = 0.48 microns

Surface Area per gram = 5.1 square meters

Surface Area per cc = 12.5 square meters

Fig XV

Particle Size Distribution Curve
for
Cerise Toner

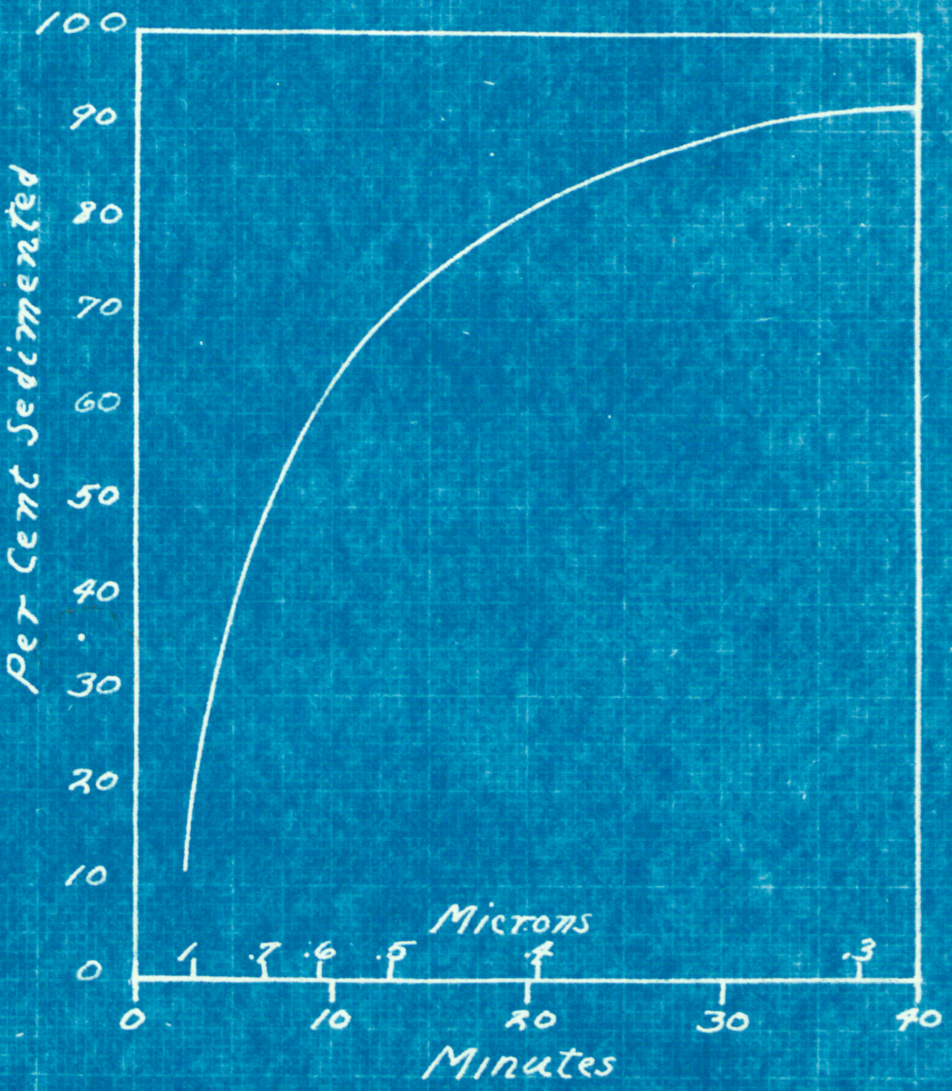


TABLE XIX

SPECIFIC SURFACE AND PARTICLE SIZE OF PEERLESS BLACK

Water Vapor Adsorption Method

Sample No.	Specific Surface (m^2/g)	Particle Size (microns)
1.	260.0	0.011
2.	131.8	0.015
3.	117.0	0.025
4.	281.0	0.010
5.	151.2	0.019
6.	41.2	0.070
7.	124.8	0.024
8.	204.6	0.015

TABLE XX

SPECIFIC SURFACE AND PARTICLE SIZE OF SUPER CARBOVAR

Water Vapor Adsorption Method

Sample No.	Specific Surface (m^2/g)	Particle Size (microns)
1.	80.8	0.0372
2.	87.0	0.0345
3.	99.3	0.0320
4.	79.2	0.0379

Fig XVI

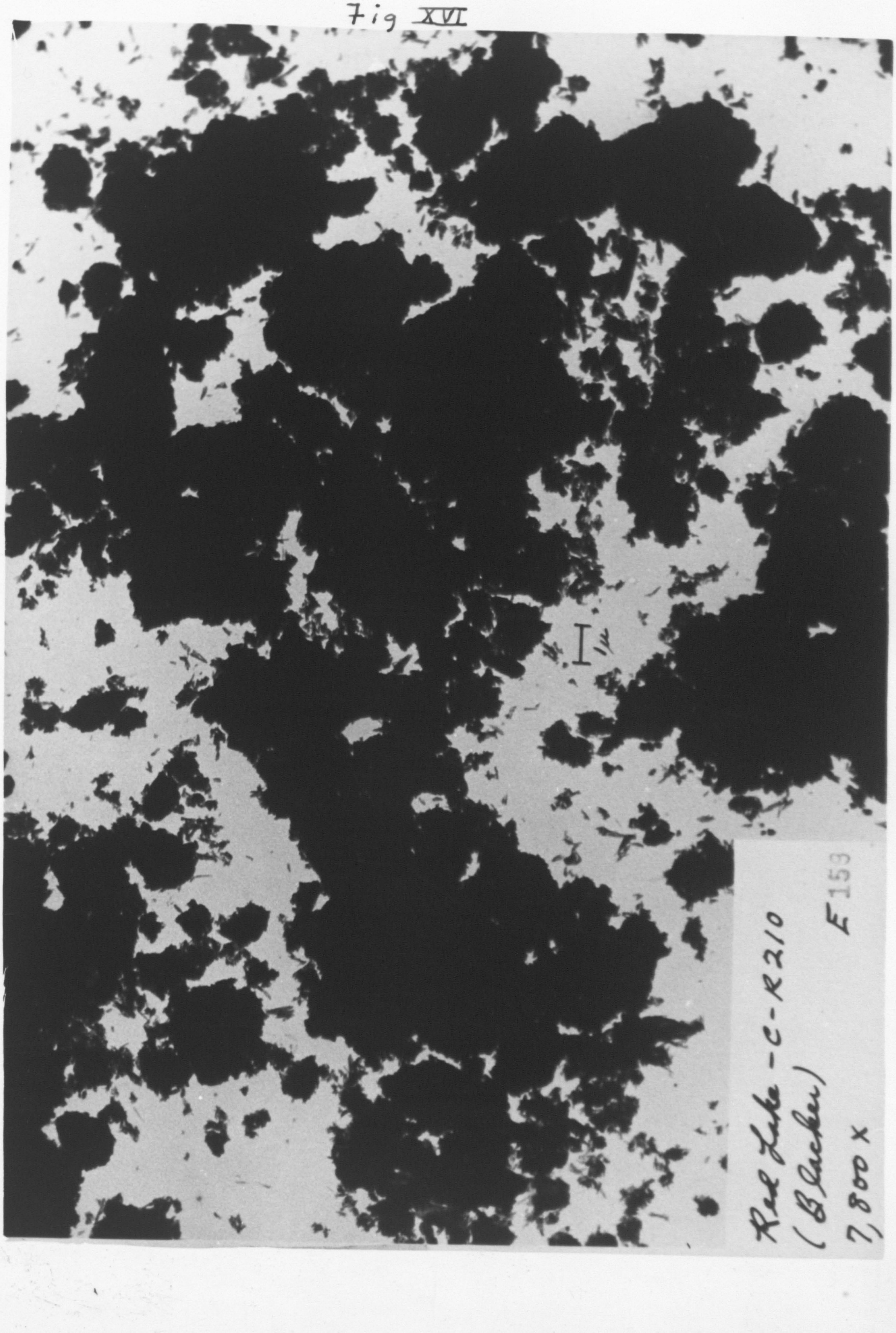


Fig XVII

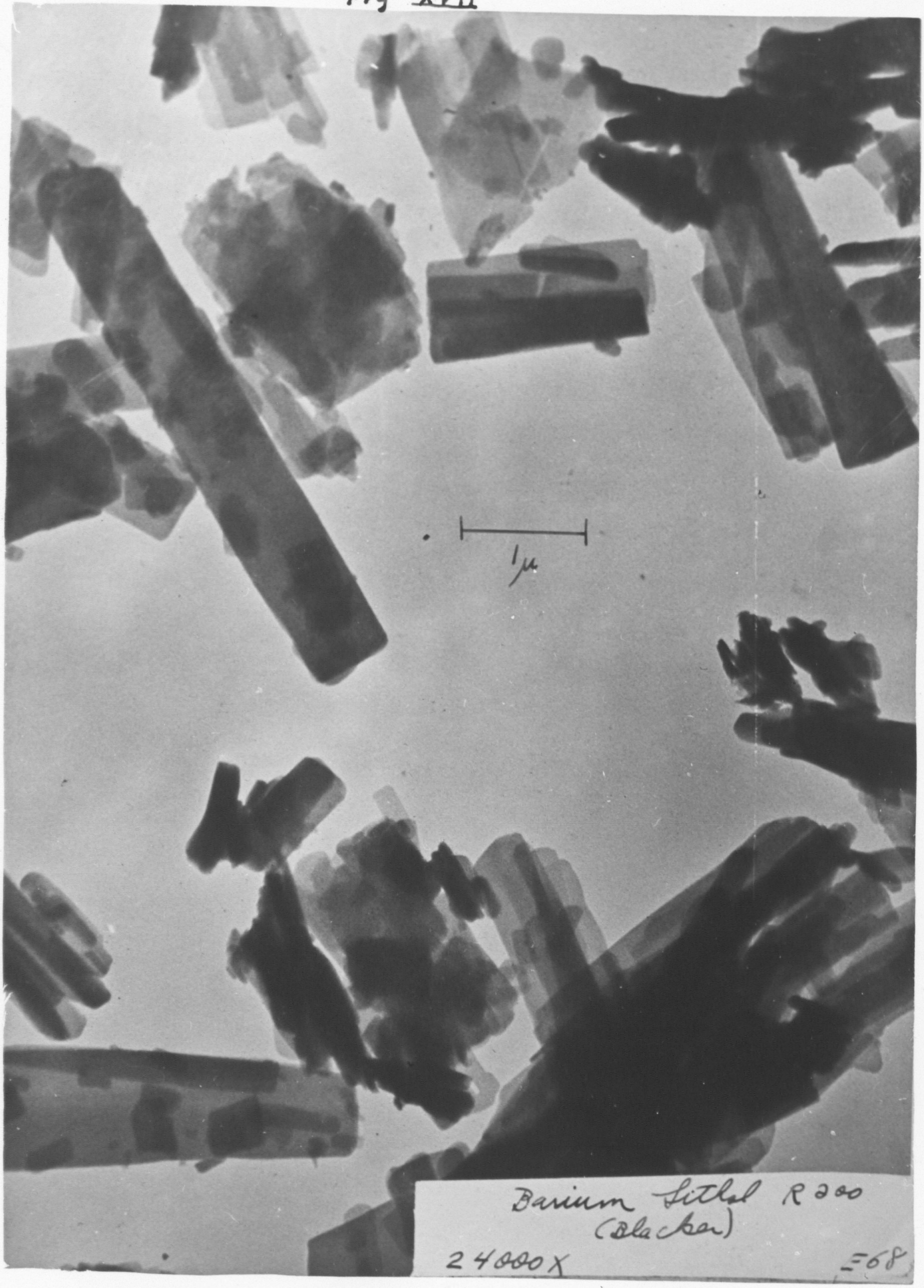


Fig XVIII

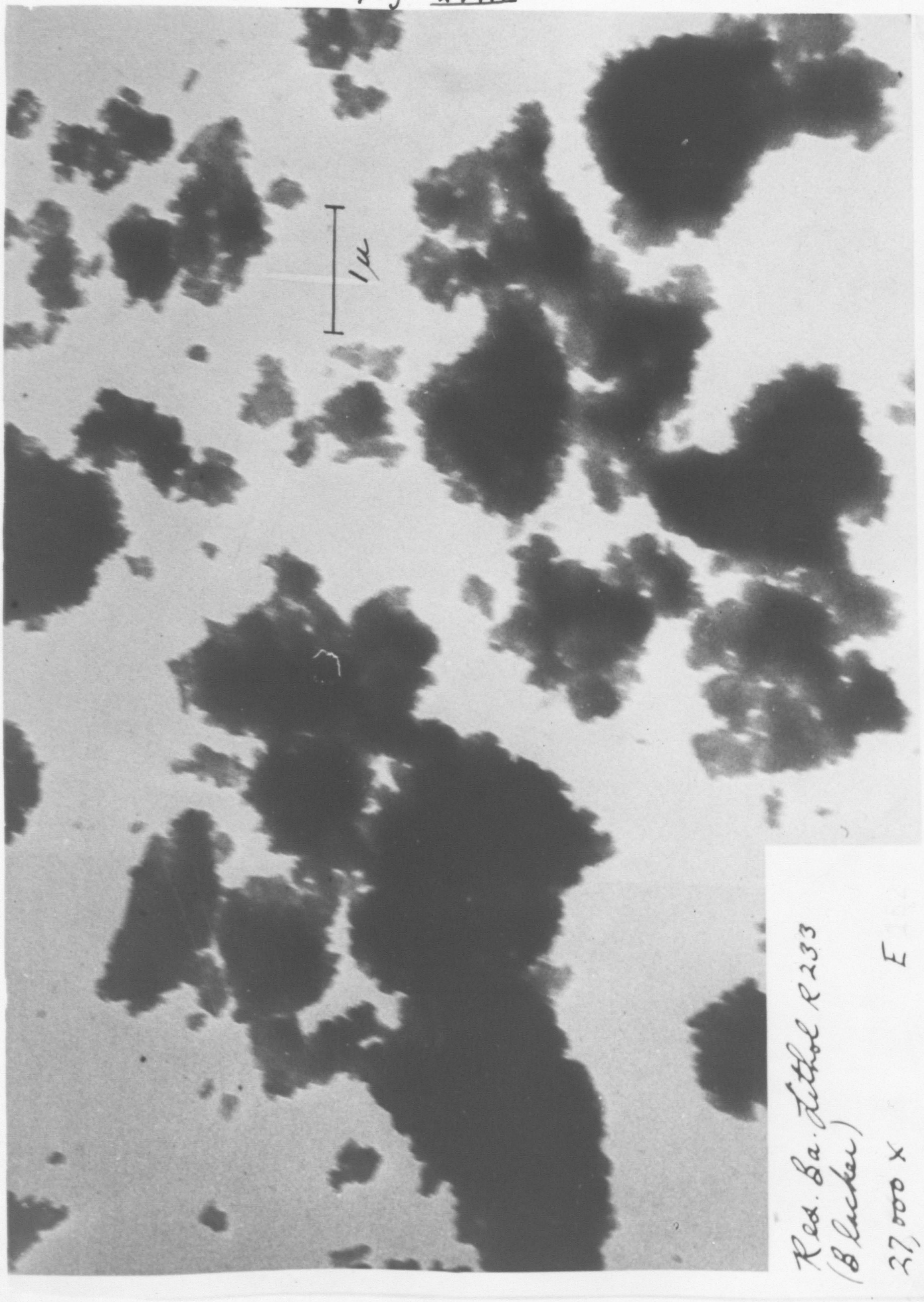
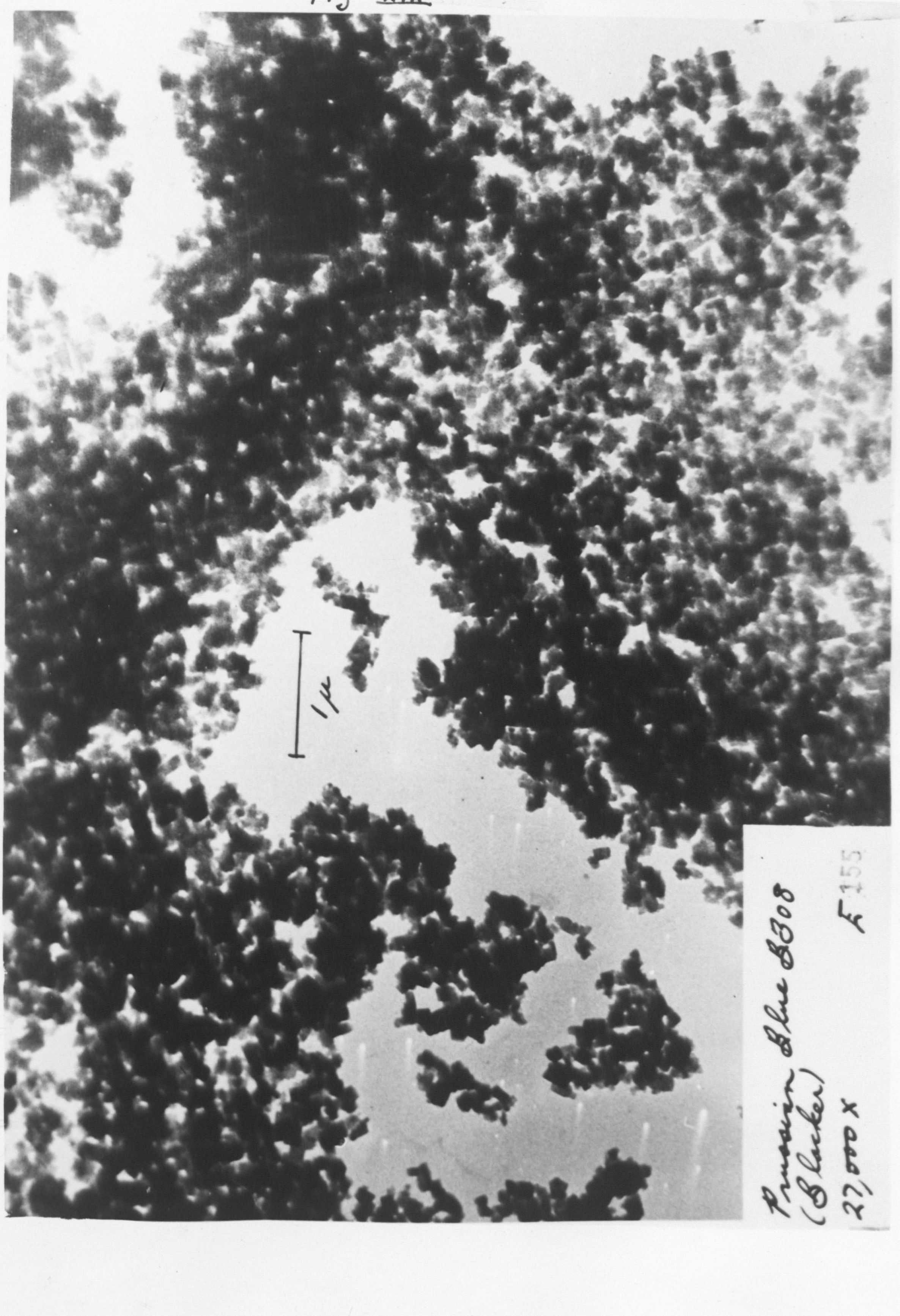


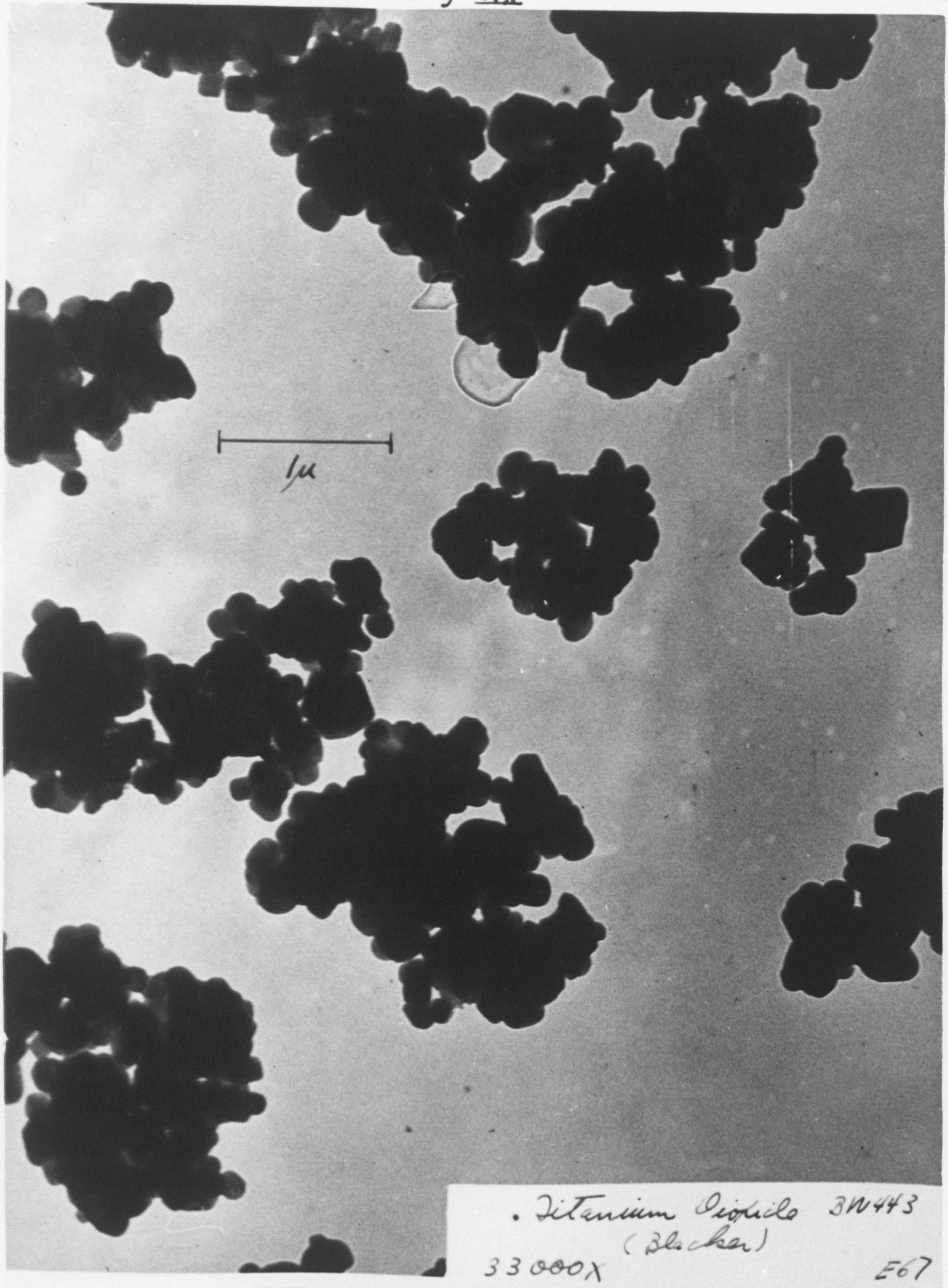
Fig XIX



Prussian Blue B308
(Blacker)
27,000 x

F 155

Fig XX



. Titanium Dioxide BW443
(Blacker)
33000X
E67

Fig XXI

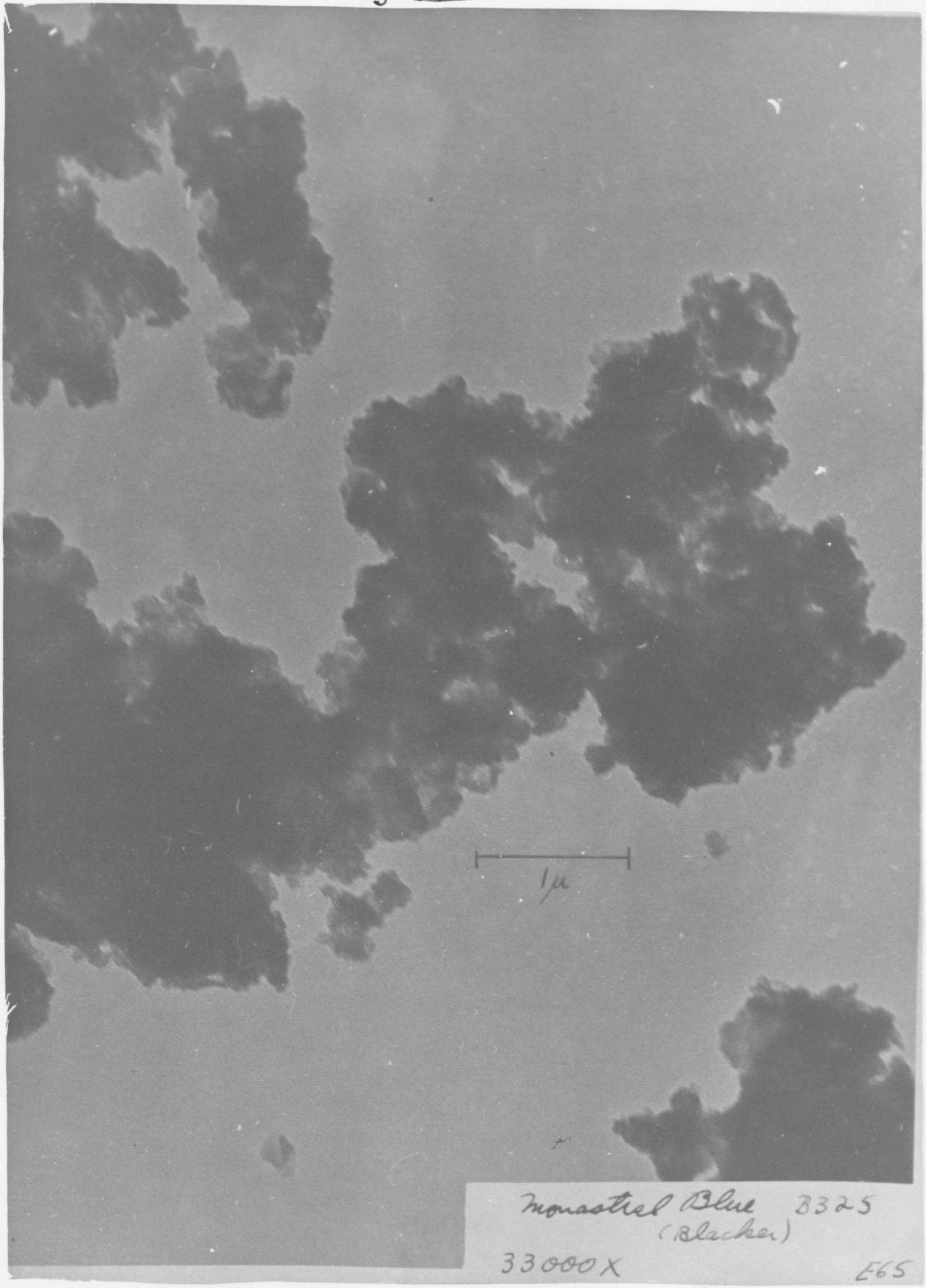
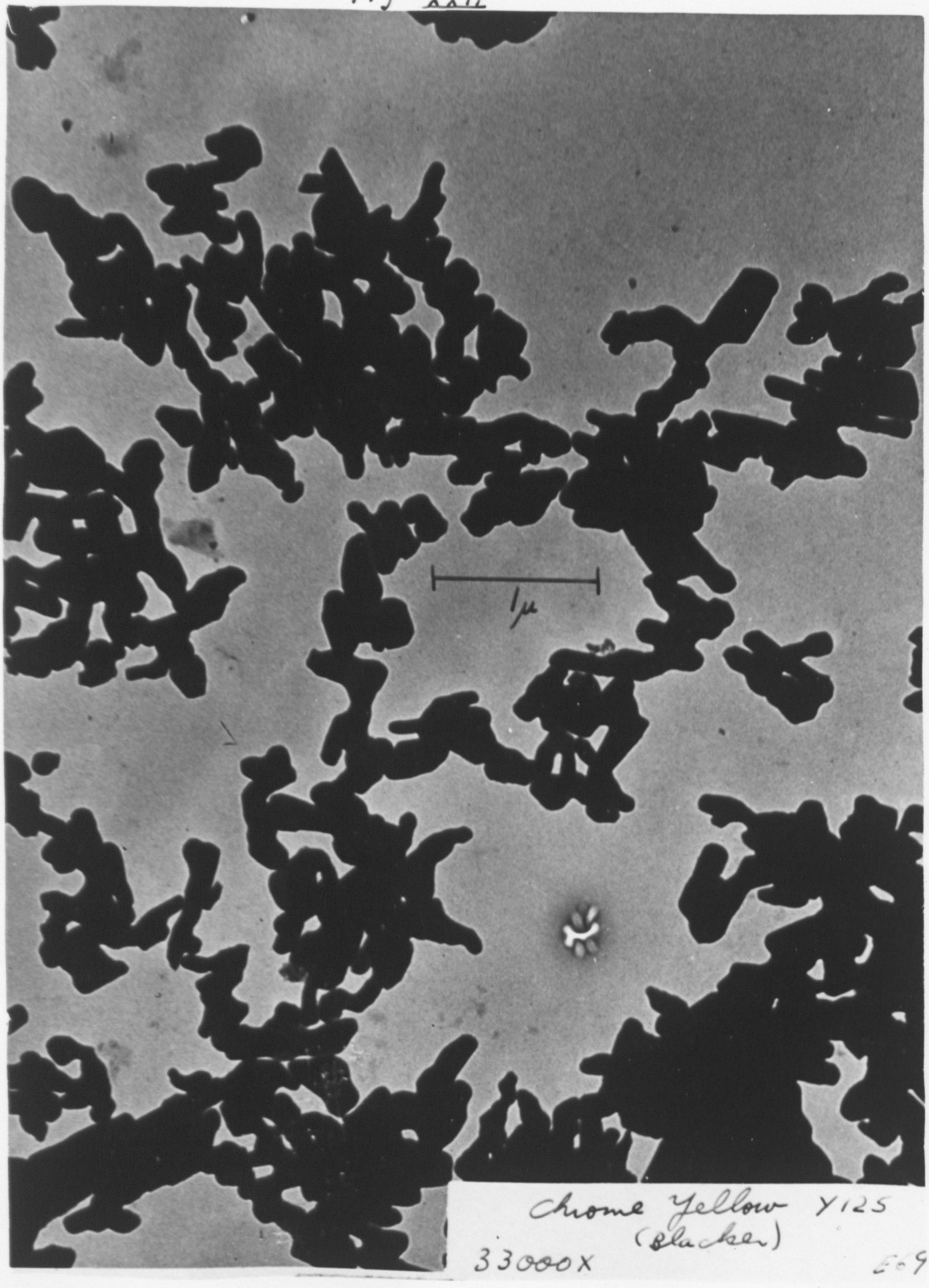
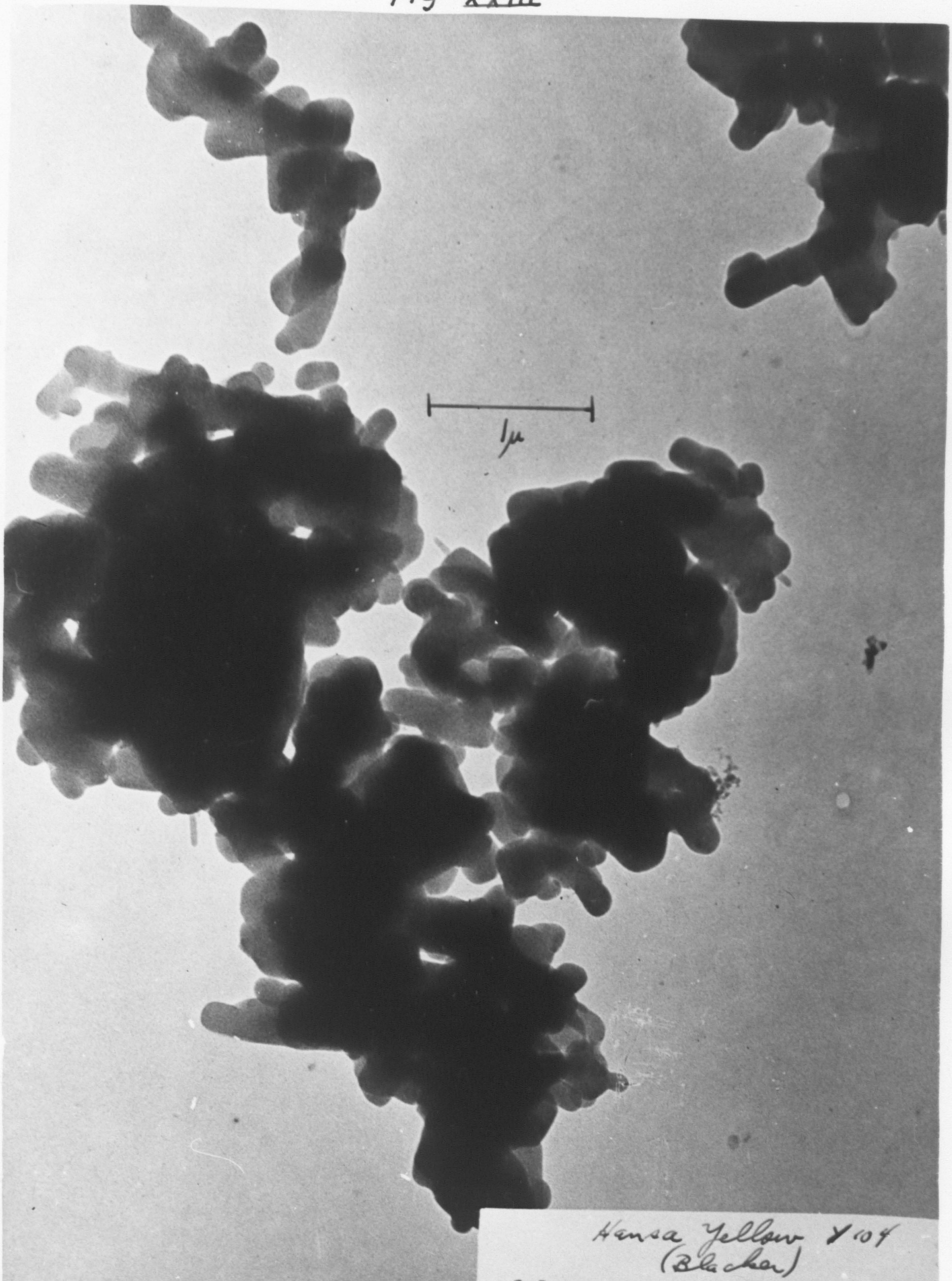


Fig XXII



Chrome Yellow Y125
(Blacker)
33000X
E-9

Fig XXIII

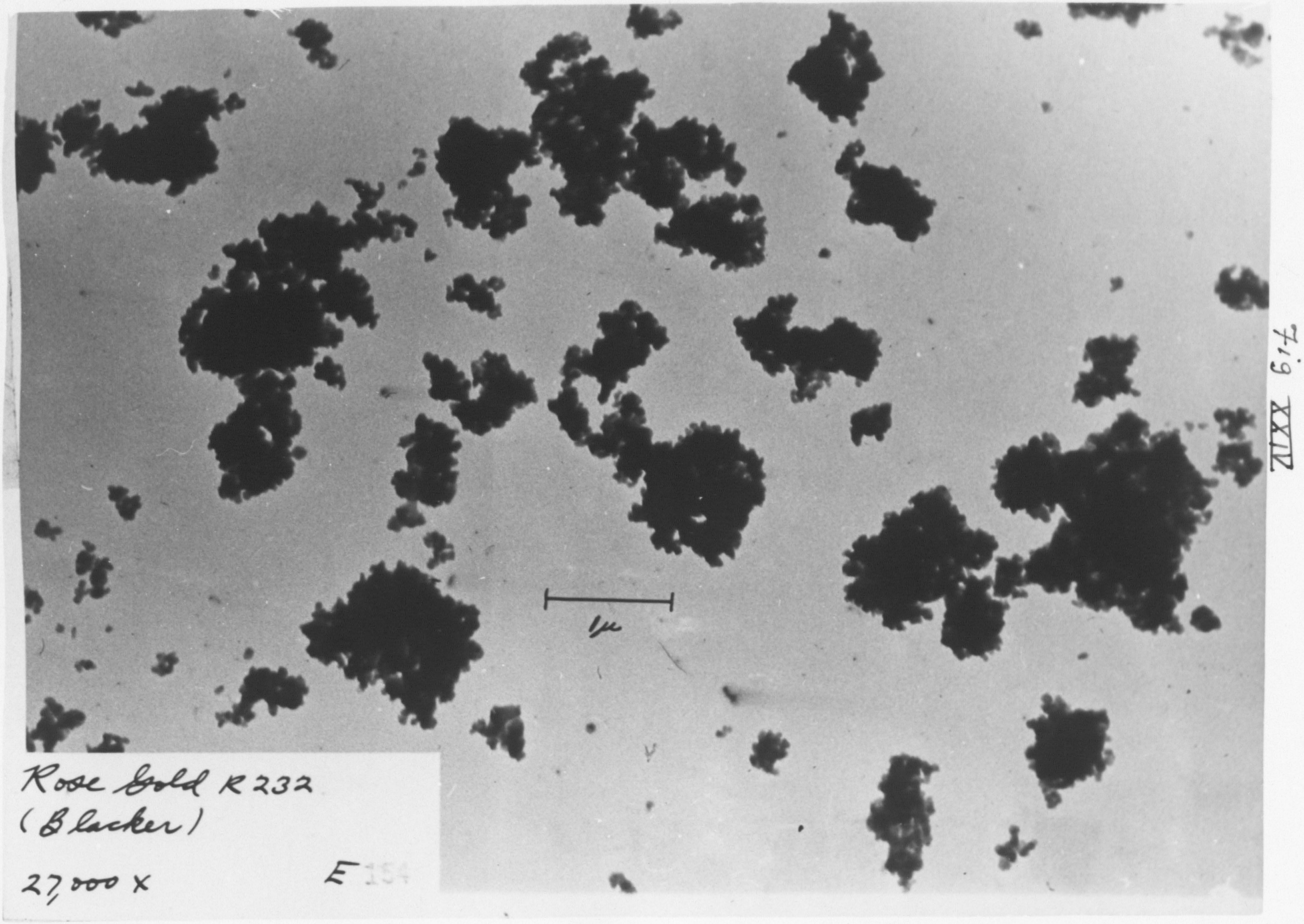


Hansa Yellow Y104
(Blacker)

33000X

E70

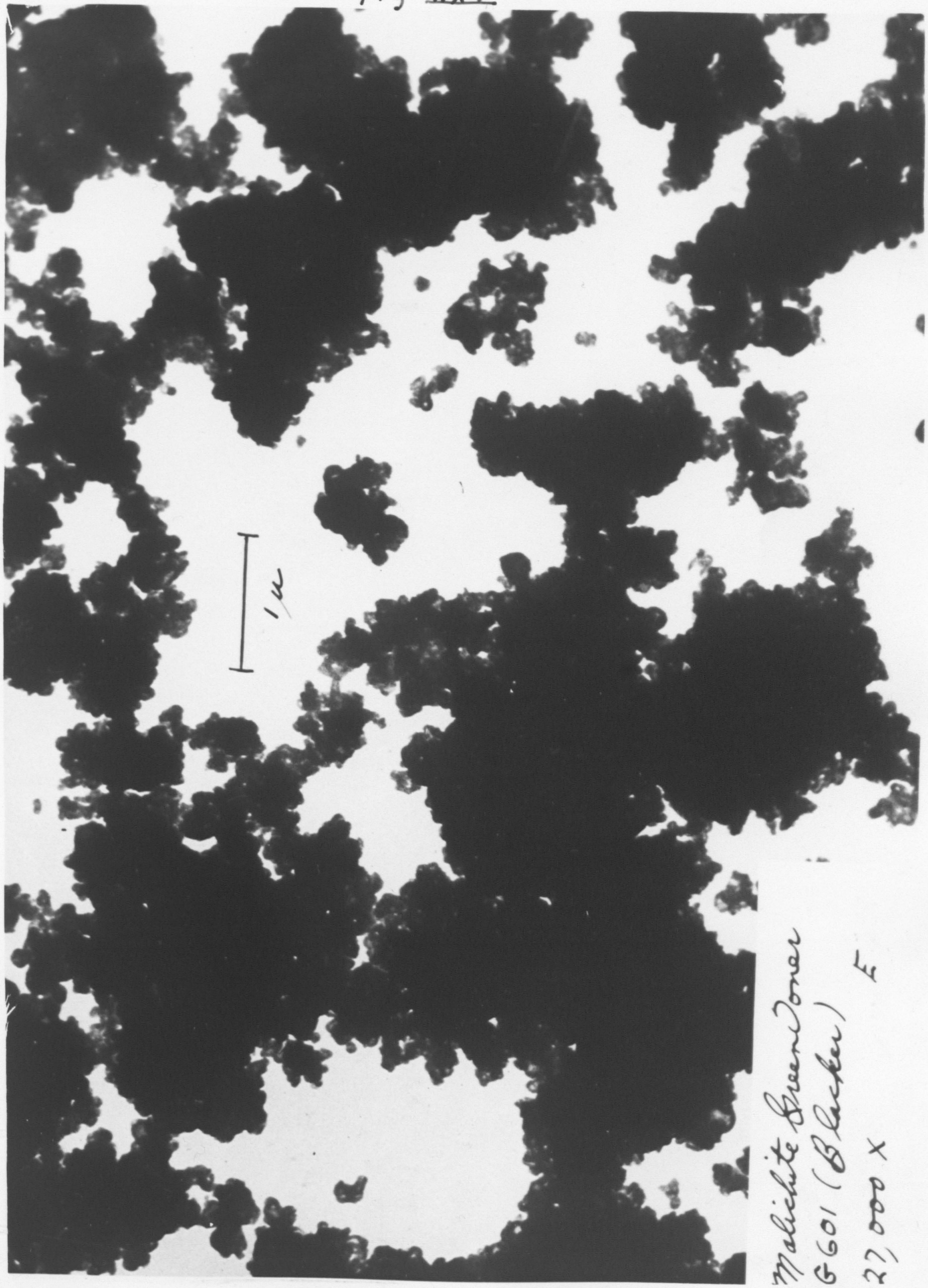
Fig XXIV



Rose Gold R 232
(Blacker)
27,000 x

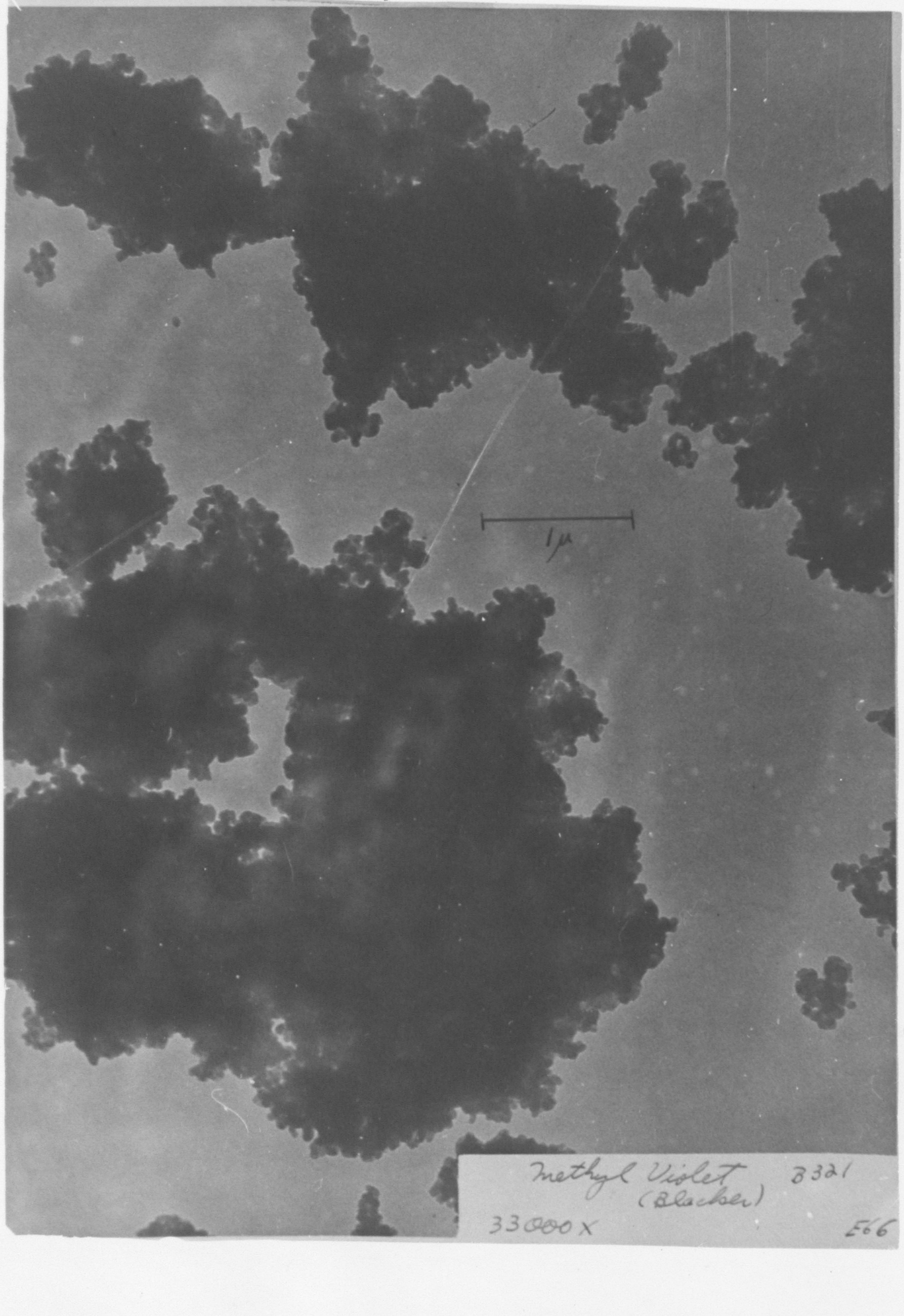
E 154

Fig XXV



Malichite Green Toner
G601 (Blacker)
27,000 X
E

Fig XXVI



Methyl Violet B321
(Blacker)
33000X E66

Fig XXVII

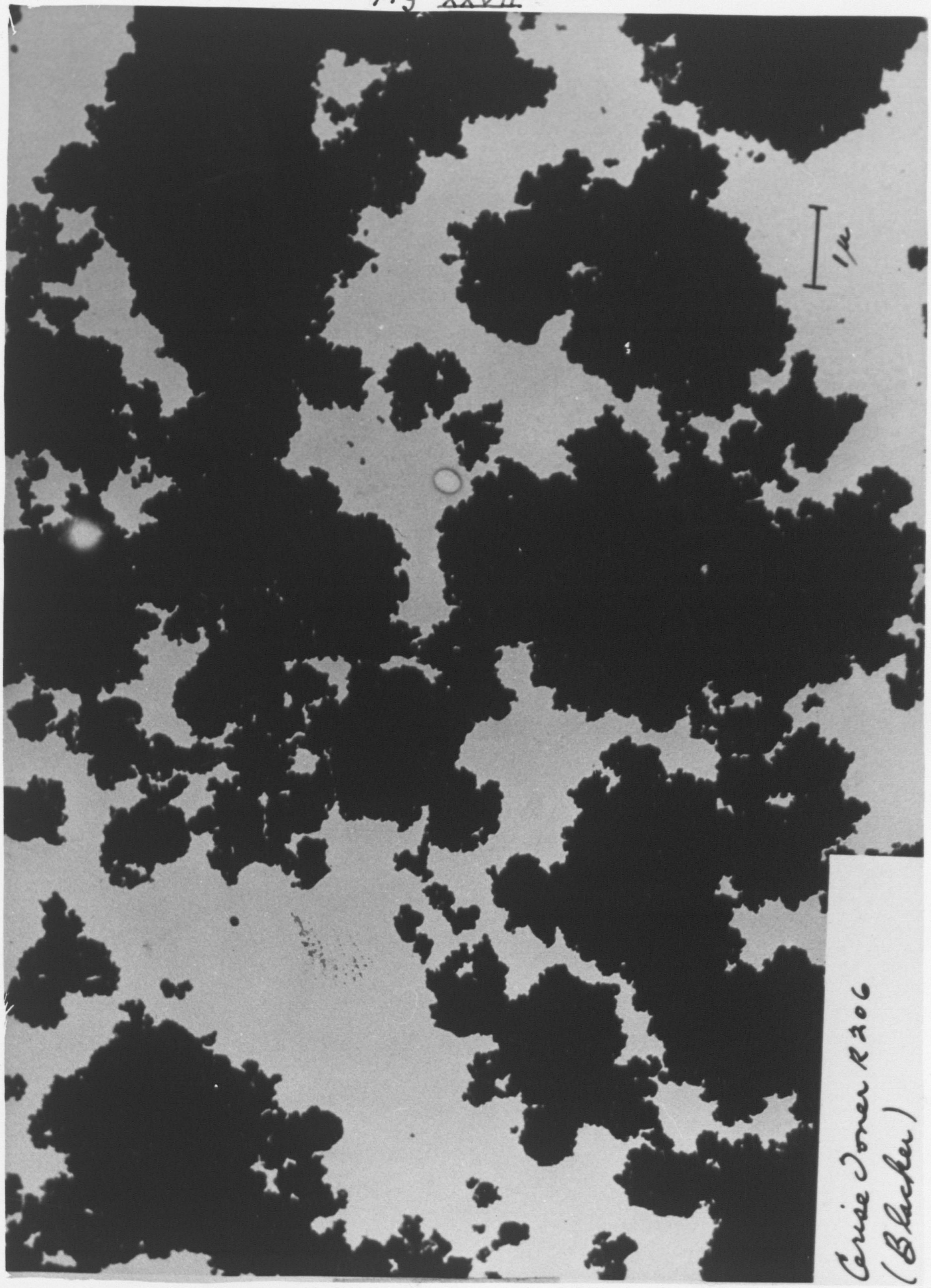


TABLE XXI

COMPARISON OF THE RESULTS OF THE SEDIMENTATION, VISUAL MICROSCOPIC, AND ELECTRON MICROSCOPIC METHODS OF PARTICLE SIZE DETERMINATION

Pigment	Average Diameter by Sedimentation Method	Average Diameter by Visual Microscopic Method	Average Diameter by Electron Microscopic Method
Red Lake C	----	---	0.8
Barium Lithol	0.94	0.2	3.0
Resinated Barium Lithol	0.26	< 0.2	0.3
Prussian Blue	----	< 0.2	0.3
Ultramarine Blue	0.25	0.2	---
Titanium Dioxide	----	0.4	0.3
Monastral Blue	0.99	< 0.2	0.2
Chrome Yellow	0.25	0.5	0.3
Hansa Yellow	----	1.0	1.0
Chrome Green	0.10	0.4	---
Rose Toner	0.48	0.4	0.1
Malichite Green	----	0.2	0.3
Methyl Violet Toner	0.28	< 0.2	0.1
Cerise Toner	0.48	0.3	0.4

5. Effect of Pigment Particle Size on Ink Drying Time

In this part of the thesis an attempt was made to determine the effect of pigment particle size on ink drying properties. Fourteen different pigments were selected, carefully including many different pigment types, pH values, particle size ranges, and varying degrees of chemical reactivity. These pigments were used to pigment fourteen different printing inks, the drying data of which were obtained and reported in part two (Table V) of the experimental work. A complete description of the experimental procedure of this work has already been given in part two and will not be repeated here.

These fourteen pigments were then submitted to three different methods of particle size determination and their particle sizes accurately determined. The experimental techniques used in these methods are fully described in part four of the experimental work. The results obtained are given in Table XXI.

Having obtained drying and pigment particle size data on these pigments it was hoped that a correlation between pigment particle size and ink drying time could be demonstrated. It will be noted that there are many factors other than pigment particle size influencing the drying properties of the inks studied. Regardless of this complication, however, it was considered reasonable to expect to obtain data that would indicate that pigment particle size is a factor influencing the drying properties of printing inks.

The second part of this work was an attempt to remove as many variables as possible other than pigment particle size. This was accomplished by obtaining from the Godfrey S. Cabot Company a series of carbon black pigments varying markedly in pigment particle size but only slightly in chemical composition and pH. Inks of the following composition were made using each of these pigments:

20% carbon black pigment
80% Sinclair & Valentine No. 3 varnish
4% cobalt naphthenate drier containing
6% cobalt as metal.

Each ink was ground twice over the mill with drier present. Drying tests were then run on Duplex Super Varnish paper at relative humidities of 43, 62, and 76%. The results of this work are given in Table XXII and in Figure XXVIII.

If the results tabulated in Table V are examined as a whole, and the drying data of the known oxidizing pigments eliminated, it is seen that a correlation exists between pigment particle size and drying time. If the drying data without drier is considered it is seen that the pigments of small particle size generally produce slow drying inks, whereas, the pigments of large particle size produce rapidly drying inks. Unfortunately the value of this is reduced by the complicating factor of varying pigment pH.

There is some evidence, however, that pigment particle size controls the ink drying properties to some extent. For example, methyl violet toner has the smallest particle size measured and has the longest drying time of any of the pigments studied although it is not the most acid pigment. Cerise toner has the lowest pH, but its particle size is four times as large as methyl violet toner. Malichite green also produced a rapidly drying ink despite its acid reaction. Monastral blue produces a slow drying ink even with its alkaline properties. This is probably due to its very small particle size.

The results tabulated in Table XXII and graphed in Figure XXVIII are much more satisfactory. The complicating factor of chemical activity of the pigment and widely varying pH has been removed to a very large extent. The pH of the series of carbon black pigments studied has been held within three pH units. Figure XXVIII illustrates a rather good correlation between pigment particle size and ink drying times. It is important to note that the difference in pigment pH does not appear to complicate the data obtained.

An attempt to offer a theory to explain the effect of pigment particle size on the drying properties of the resulting printing inks is extremely difficult because of the numerous conflicting ways in which pigment particle size may influence drying.

The most popular theory is that the smaller the particle size, the greater the pigment surface area, and the greater the drier adsorption on the pigment surface. It is difficult to explain, however, why the pigment particle should selectively adsorb cobalt naphthenate drier when relatively large quantities of polar, free fatty acid is available. Also, if the cobalt drier acts catalytically in transferring the oxygen molecule from the atmosphere to the oil molecule, it is hard to believe that supporting this catalyst on a pigment of huge surface area would greatly impede the drying action. A further objection is that some pigments of extremely small particle size, but of high pH are rapid drying.

There is, however, some evidence that in the particular case of carbon black pigments, drier is adsorbed to a large extent on pigments of greater surface area. Therefore, until further evidence is obtained, the drier adsorption theory might be offered as a tentative explanation of this phenomenon.

A second theory which may be offered is that if the pigment presents a catalytically active surface, and there is every reason to believe it does, the greater the surface, the more effective this action will become. If the pigment has an acid reaction, it is reasonable to assume that the smaller the particle size, or the larger the surface area, the more effectively this available acid is presented to the oil molecule and the more efficient its retarding action will become.

If this theory is correct, however, it could be assumed, also, that the smaller the particle size of an alkaline pigment, the more effective this alkali would become in accelerating the drying rate of the printing ink. Unfortunately the data obtained in this work is not sufficiently complete to substantiate this assumption.

The following conclusion may be drawn from the data obtained in this section of the thesis:

1. In general, the rate of drying of lithographic ink decreases with decreasing particle size of the pigment used.

TABLE XXII

EFFECT OF PIGMENT PARTICLE SIZE ON THE DRYING OF LITHOGRAPHIC INKS

* Pigment	Particle Size microns	Surface Area M^2/g	pH/	Ink Drying Time in Hours 43% R.H.	62% R.H.	76% R.H.
A	0.036	832	2.4	43.+	43.+	43.+
B	0.041	733	2.6	31.3	43.+	43.+
C	0.055	542	2.9	11.5	13.8	23.7
D	0.079	376	5.6	4.8	5.3	6.7
E	0.088	334	5.0	5.7	5.6	7.3
F	0.102	294	4.9	5.4	6.0	7.1
G	0.136	220	4.3	4.4	5.2	6.0
H	0.314	96	4.2	4.1	5.1	4.9

* Carbon black pigments supplied by Godfrey Cabot Company

/ pH given by Godfrey Cabot Company

EFFECT OF PIGMENT PARTICLE SIZE ON INK DRYING TIME

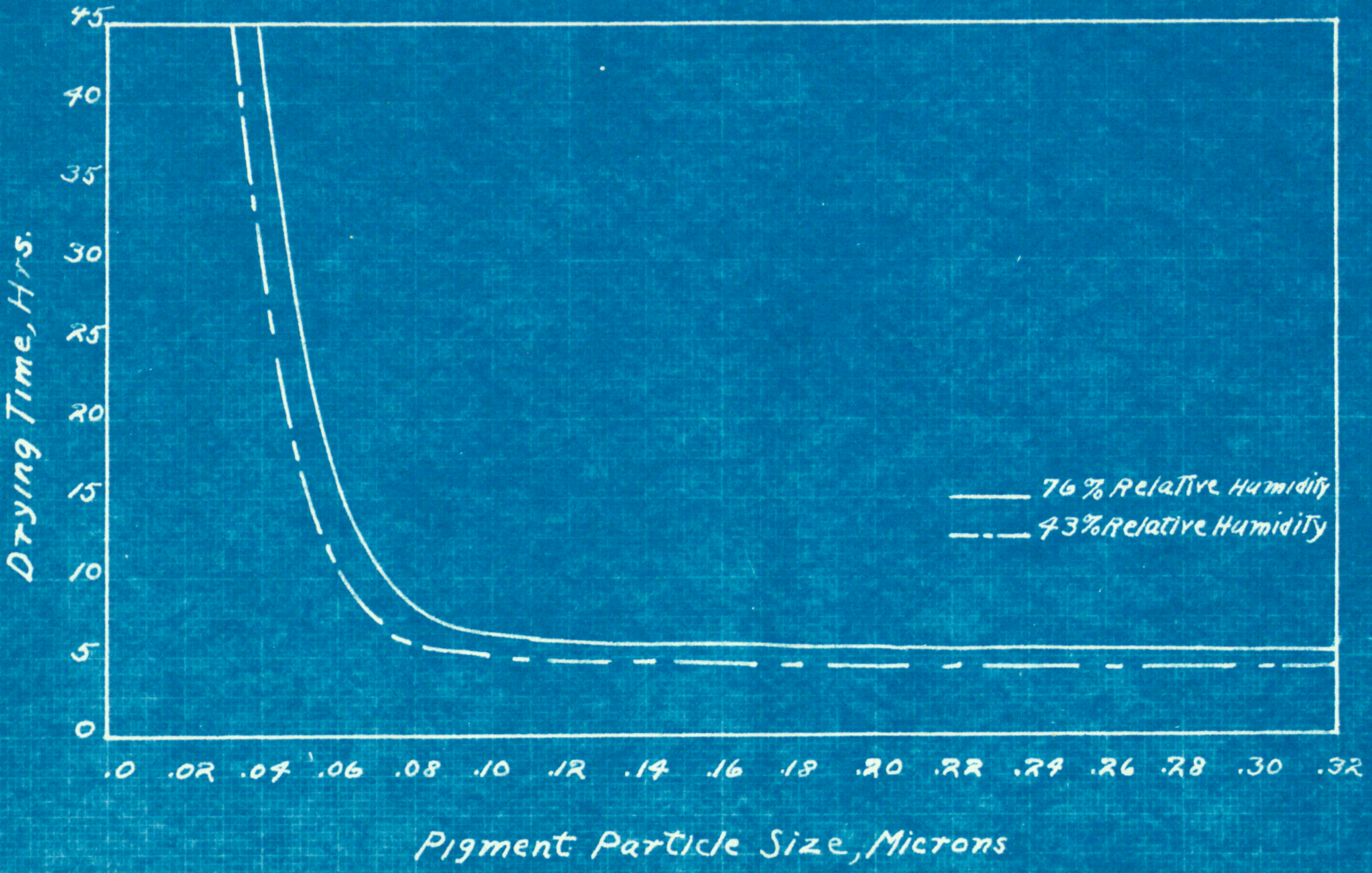


Fig XXVIII

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