THE SIZE FREQUENCY DISTRIBUTION OF PARTICLES OF SILVER HALIDE IN PHOTOGRAPHIC EMULSIONS AND ITS RELATION TO SENSITOMETRIC CHARACTERISTICS

BY E. P. WIGHTMAN AND S. E. SHEPPARD

I. Introductory Paper

Although the existence of some relation between size of grains in a photographic emulsion and the sensitiveness of the emulsion was accepted early,[1] little or no attention appears to have been paid to the variation in grain size in one and the same emulsion or layer, as a factor in the photographic properties. Attention was first called to this by C. E. K. Mees,[2] in a paper on "The Physics of the Photographic Process." He considers that, "inasmuch as the emulsions are not homogeneous, but each emulsion will contain grains of all sizes, the sensitiveness will depend upon the distribution

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[1] J. Gaedicke: Eder's Jahrbuch. Phot., p. 209 (1895); Eder's Handbuch. Phot., 3, 66 (1903).

A. P. H. Trivelli in 1911 (Zeit. wiss. Phot., 9, 168), had considered a certain relationship to exist between the size of grains of silver halide and the energy absorption when light falls upon them. Liesegang (Phot. Korr., 47, 468), in the same year, stated that size of grain is concurrent with sensitiveness and is limited by visible granularity of the negative. Koch and du Prel (Phys. Zeit., 17, 536) in 1916 also made some important observations tending to show that the so-called coarse grained plates are not necessarily the most sensitive. Recently, Slade and Foy (Proc. Roy. Soc., 97A, 181 (1920)) have made some careful spectrophotometric measurements of the absorption of light by silver bromide. Further, a very recent article by R. E. Slade and G. I. Higson (Proc. Roy. Soc., 98A, 154 (1920)) deals with the action of light on a dilute emulsion, which was said to have grains of uniform size and was one layer thick. Others have likewise given thought to the questions of the size of grain and sensitiveness and of the absorption of light by the silver halides. A more complete bibliography of this subject will be presented in a forthcoming monograph on the photographic theory by A. P. H. Trivelli and S. E. Sheppard.

[2] C. E. K. Mees: Jour. Franklin Inst., 179, 141 (1915).

of the different sizes of grains, as also will the shape of the
plate curve, this plate curve being the relation between den-
sity and logarithmic exposure." Further, he states "the
shape of this curve depends to a considerable extent on the
distribution of the different sizes of grains in the emulsion.
With a homogeneous emulsion we should have a simple curve
with a short over and under exposure portion, as shown in
Fig. 1, and by adjusting the sizes of grain so that there is a
sufficient number of grains distributed around the mean, we
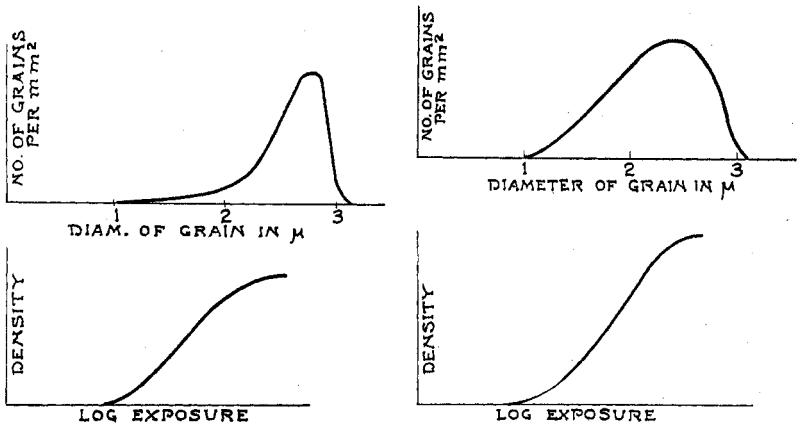can diminish the size of the under exposure position to obtain

Fig. 1

Fig. 2

a longer straight line (Fig. 2). We can therefore form a
mental picture of the relation between the distributions of the
grain and the sensitiveness curve." The author points out
that up to that time there had been very little experimental
work on this subject, and that the relations suggested were
speculative. It appears that the main suggestion is that a
proportionality exists between the degree of heterogeneity
of the grains, otherwise the breadth of the frequency curve,
and the latitude of the plate or emulsion. It is stated that
any such considerations are to be regarded as limited to high
speed emulsions.

In this connection we should point out that a first result of our experimental work is to show that the frequency curve alone is of less value in relation to the sensitometric curve than the projective area curve obtained by plotting the product of frequency by the projective area of grains of a given class against the corresponding classes. This will be discussed more fully later. It seems desirable, however, to call attention to this point at this stage.

Experimental investigation of the problem was begun in June, 1919, later papers give account of the results. Meanwhile there has appeared a paper by Slade and Higson,[1] and another by T. Svedberg,[2] in which the same problem is envisaged.

Slade and Higson state that "under ordinary conditions of exposure, the shape of the plate curve (as determined by Hurter and Driffield's method) is dependent on:

"(1) The relation of the different sizes of grains in the plate to each other and the quantity of each present.

"(2) The thickness and capacity of the film.

"(3) The time and method of development (though on 'infinite' development almost the same result is obtained whatever the developer and however much bromide it contains)."

They emphasize the importance of the first factor and show by H. and D. curves the difference between a plate with grains nearly of the same size and a plate with grains of mixed sizes. They also give photomicrographs which illustrate the two kinds of plates. The plates with grains of nearly uniform size have much steeper curves than those with mixed grains.

Their results are obviously only semi-quantitative, as no measurement of the dispersity of the silver halides is given. From the curves it appears that according to their view γ_∞ is increased by homogenizing the grain, and latitude, i. e., the projection of the straight line part of the plate curve, is

[1] R. E. Slade and G. I. Higson: Phot. Jour., **59**, 260 (1919).

[2] T. Svedberg: Zeit. wiss. Phot., **20**, 36 (1920).

diminished. In partial agreement with this is Lüppo–Cramer's[1] statement that plates of homogeneous grains, prepared by after-peptization of a finished emulsion, show a much earlier reversal period than plates with non-uniform grain.

In a quite recent paper by F. E. Ross,[2] of this Laboratory, on the relation between photographic density and exposure the author develops a new theoretical formula for the characteristic curve. It is pointed out that many formulae can be constructed depending upon particular assumptions of the following types:

a. Relative frequency of grains of varying size.

b. Relative sensitiveness of grains of varying size.

c. Variation of grain sensitiveness with light-intensity and wave-length for each class of grains.

d. Ratio of inert to active grains, depending on grain size.

e. Number of layers of silver halide.

f. Opacity of emulsion and its variation with wave-length.

The author points out that data for weighing these assumptions severally are lacking, hence, it is unprofitable to develop a formula on any but the simplest assumptions. As these he takes:

1. All grains in an emulsion are divisible into n groups, each group as a whole obeying the mass action law.[3]

2. The silver mass the same for each group.

3. The sensitivity factor of the groups arrayed in geometrical progression. This regards as equivalent true sensitivity difference (inherent) and apparent sensitivity differences (topical) due to thickness of emulsion. This equivalence is possible on account of the reciprocal equivalence of intensity and absorption-coefficient in a layer.

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[1] Lüppo-Cramer: Photographische Probleme, Halle, 1907.

[2] On the Relation between Photographic Density, Light Intensity and Exposure Time, by F. E. Ross: Jour. Optical Soc. America, 4, 255 (1920).

[3] That is, the law that rate of reaction is proportional to mass of material unchanged:

$$\frac{dx}{dt} = k\mathrm{I}\,(A - x).$$

From these assumptions a formula is derived. Calling d_m the maximum density for infinite exposure (reversal neglected), k the sensitivity factor, R the common ratio of the sensitivities of the groups, the equation is obtained

$$D = d_m \left(1 - \frac{1}{n} \sum_{s=0}^{s=r-1} e^{-Rr^s I t}\right)$$

Taking values $r = 1/2$ and $n = 1, 2, \ldots 10$ the field of practical emulsions should be well covered. A series of typical curves thus obtained are shown in the figure.

Now it will be noticed that for increasing values of n the slope, or γ_∞ becomes less and the straight line portion longer. Instead of the H. and D. latitude Ross takes the "range," as antilog of the projection of the line AA' or BB' (Fig. 3) on the exposure axis, as measure of the reproducing
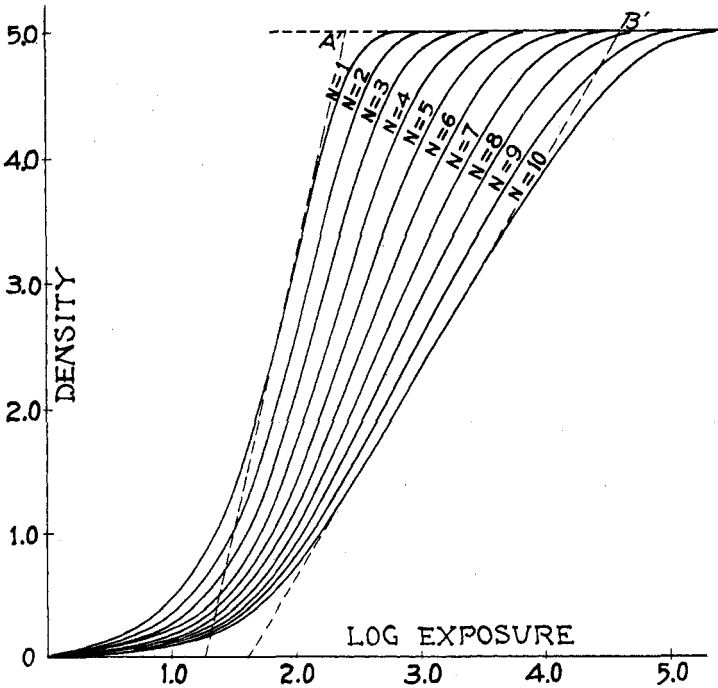

Fig. 3

power of an emulsion.   The "range" increases with n as shown in following table:

n	Range
1	15
2	17
4	35
8	290
10	1000

Although n does not refer explicitly to the number of classes of different sizes, it would do so (a) if these had varying sensibilities (b) if opacities were constant.   In this case, Ross' equation agrees partly with Mees' hypothesis that increasing grain heterogeneity increases latitude,[1] but also agrees with Higson and Slade's contention that more homogeneous grained emulsions have steeper curves.

We may point out here, anticipating certain results given in a later paper, that the influence of size of grains is not symmetrical in respect of their effect on exposure conditions (light intensity gradient) and development results (development factor).   A great number of very small grains may contribute little on development to effective density, but they may very markedly affect the turbidity and opacity of the plate or film; hence their effect on the characteristic curve is not revealed by the density after development.

Slade and Higson were apparently ignorant of Mees' previous paper, and this is also the case with Svedberg.   The latter considers that the problem at issue may be treated as, generally, relation of light sensitiveness to size of grain, and specifically, the four following cases of this:

(1) Every single grain has the characteristic curve of the plate.

(2) For every class of grains of nearly the same size in the emulsion there is a distinct curve.

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[1] Latitude being analogous to Ross' range.

(3) The characteristic curve is only shown by emulsions with non-uniform grain.

(4) The relation between density and exposure expressed in the plate curve is a consequence of inhomogeneity of the photochemical illumination inside the photographic layer.

The last case is discounted largely by results with very thin layers previously obtained by Lüppo-Cramer and W. Scheffer,[1] and confirmed by Svedberg. As to the first case, Svedberg concludes, in agreement with Sheppard and Mees, that "reactivity" (rate of reduction) of the grain depends on exposure, but not absolute reducibility. Hence, the problem falls back on the second and third cases. It is pointed out that these require statistics of distribution of size in relation to exposure on ultimate development. Instead of measuring the reduced grains, of distorted appearance, Svedberg has applied the method of difference determination. Statistical measurements of grain size (or dispersity) are made first in the unexposed but developed emulsion, after treatment with a silver solvent, then they are made for a series of exposures. From these measurements two important diagrams are obtained, namely, (a) the curves connecting exposure and percentage reduced grains for each order of magnitude of the grains, (b) curves showing relation between size of grain and percentage made reducible after a certain exposure.

The first type of curve is comparable with the characteristic curve (since the number of grains is a factor in density). The second gives the relation of light sensitiveness to size of grain. The determination and division of sizes of residual grains was made by direct projection and microphotography of the exposed, developed layers of very thinly coated much diluted emulsion,[2] after dissolving of the developed grains. They were photographed at 1000 diameters, and then copied on paper at 4×, giving 4000× in all, and the mean *diameters* of circular grains were determined, and the projective areas of

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[1] W. Scheffer: Zeit. Elektrochemie., **14**, 489 (1908).

[2] First should be determined the effect of dilution and thickness of coating on the plate curve.

the polyhedral grains were found by means of a millimeter network. All sizes were then reduced to projective areas, and divided into four classes of magnitudes.

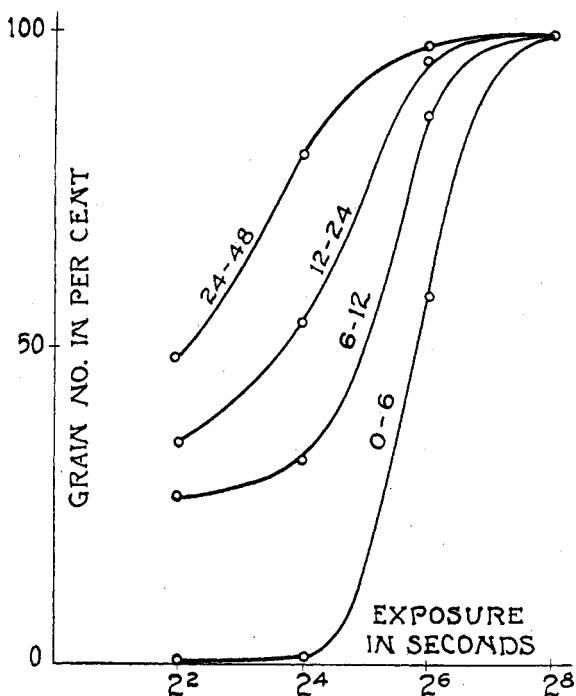The results are shown in the curves in Figs. 4 and 5.

Fig. 4

From this it appears that every class of grains has its own characteristic curve; D, however, would be proportional to P_n, where n is the number of grains, P the photometric constant or factor. Now at present we do not know precisely the function $D = f(N, S)$, where N = the number of grains per mm^3, S = the magnitude. Assuming $D \infty N$, we have $D = Nf(S)$ and $f(S)$ remains to be determined. The only estimation we have of this at present is that of Higson,[1] who gives a relation between size of developed grain, and P, the photometric

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[1] G. I. Higson: Phot. Jour., **60**, 160 (1920).

constant. If we assume that the size of the developed grain, as a first approximation, is proportional to that of the original silver bromide grain, we can use Higson's values to calculate from Svedberg's data the actual D log E curves for his four classes of grains.
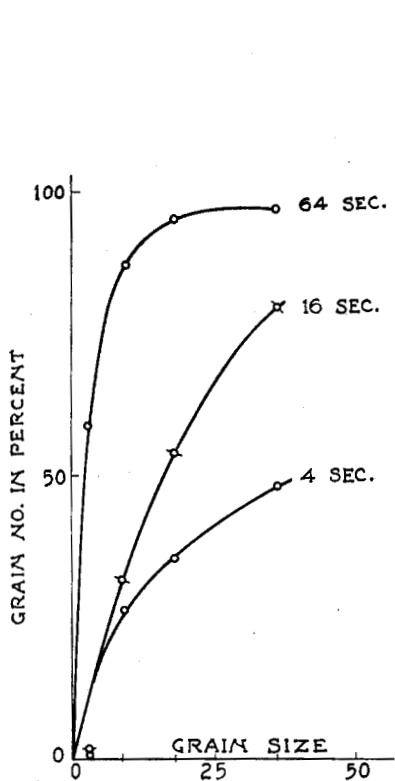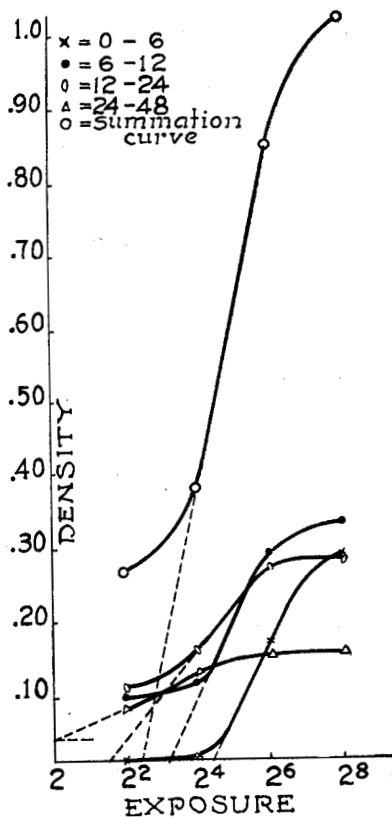

Fig. 5

Fig. 6

Table I gives the mean projective areas of the undeveloped grains for Svedberg's four classes and also these areas multiplied by four.[1] The corresponding diameters and photometric constants calculated from these are likewise given.

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[1] According to Higson the developed silver grain is larger than the original bromide particle by this amount.

TABLE I

Mean Projective Areas of Undeveloped Grains in mm² × 16 × 10⁴ Svedberg	Mean Projective Areas Undeveloped Grains in cm² = $4A$	Mean Projective Areas Developed Grains in cm² = $4A$	Mean Diams. Undeveloped Grains in cm = $\sqrt{\dfrac{A}{0.785}} = d$	Mean Diams. Developed Grains in cm = $2\sqrt{\dfrac{A}{0.785}} = 2d$	Photometric Constant $P = 61 \times 2d$
3	0.19×10^{-8}	0.75×10^{-8}	0.5×10^{-4}	1.0×10^{-4}	0.0061
9	0.56×10^{-8}	2.25×10^{-8}	0.85×10^{-4}	1.7×10^{-4}	0.0104
18	1.13×10^{-8}	4.5×10^{-8}	1.2×10^{-4}	2.4×10^{-4}	0.0147
36	2.25×10^{-8}	9.0×10^{-8}	1.7×10^{-4}	3.4×10^{-4}	0.0207
Sum	4.13×10^{-8}	16.5×10^{-8}			

TABLE II

Exposures in Seconds

4A	0	4		16		64		256	
	No. Devel. Grains	No. Developed Grains per cm² = N	Density $= 4\frac{NA}{2.3} = D$	N	D	N	D	N	D
0.75×10^{-8}	0	5.3×10^{-5}	0.0018	7.4×10^{-5}	0.0022	500×10^{-5}	0.160	850×10^{-5}	0.277
2.25×10^{-8}	0	87×10^{-5}	0.085	105×10^{-5}	0.103	286×10^{-5}	0.280	329×10^{-5}	0.322
4.5×10^{-8}	0	49×10^{-5}	0.096	75×10^{-5}	0.147	133×10^{-5}	0.260	139×10^{-5}	0.272
9.0×10^{-8}	0	18×10^{-5}	0.070	30×10^{-5}	0.117	36×10^{-5}	0.141	37×10^{-5}	0.145
16.5×10^{-8}	0	159.3×10^{-5}	0.253	217.4×10^{-5}	0.369	955×10^{-5}	0.841	1355×10^{-5}	1.016

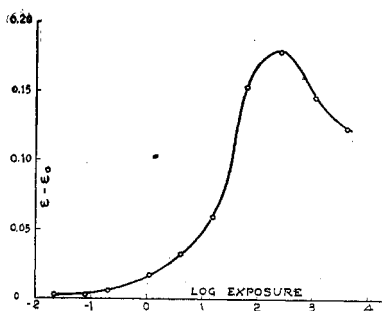Svedberg gives no data for the number of fogged grains so that these could not be taken into account in the tables. In Table II are shown (see also Fig. 6) the numbers of developed grains (exclusive of fogged grains as stated), for each exposure, together with densities to correspond (using 4A as the projective area for the developed grain), and also the additive or total densities. These total densities, it will be seen, by comparison with the total densities for the plate given in Svedberg's paper, as shown in Fig. 7 and Table III, are in the neighborhood of four times higher than those of the latter, whereas, if Higson's method of calculation is correct and if Svedberg's method is reliable, the values should agree.

Fig. 7

TABLE III
Density (= Extinction Coefficient)

Time of Exposure in seconds	Total density	Density less fog
0	$0.105 \ (= \epsilon_0)$	0
0.02	0.109	0.004
0.08	0.109	0.004
0.2	0.112	0.007
1	0.124	0.019
4	0.138	0.033
16	0.165	0.060
64	0.258	0.153
256	0.283	0.178
1024	0.250	0.145
4096	0.229	0.124

The most plausible explanation of this large discrepancy appears to be a fallacy in Higson's assumption that in general the developed silver grain has twice the diameter of the original bromide grain (i. e., 4 times the area). It is known

for instance, that certain developers, such as phenylenediamine, and hydrazine give developed grains considerably smaller than the original grain. Of course, it may be argued that these developers are not capable of giving complete development or perhaps they cause part of the silver to be dissolved. However, that may be, there does not appear to be sufficient experimental evidence for Higson's assumption. Work on this point, namely the determination of the ratio of the size of developed to undeveloped grain for various developers is much to be desired, and is about to be investigated in this laboratory by Mr. A. P. H. Trivelli.
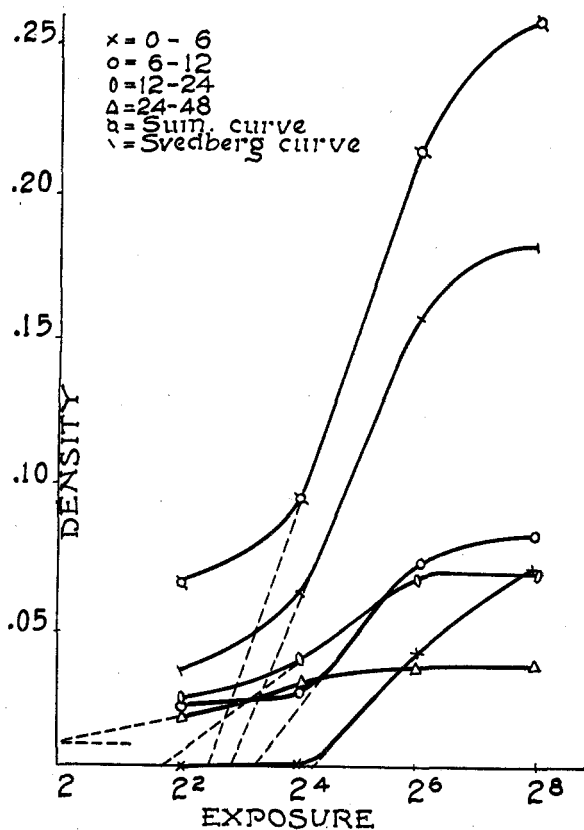
Fig. 8

TABLE IV

Exposure in Seconds

A	0	4		16		64		256	
	No. Devel. Grains	No. Developed Grains per cm² = N	Density $= \frac{NA}{2.3} = D^1$	N	D	N	D	N	D
0.19×10^{-8}	0	5.3×10^{-5}	0.0005	7.4×10^{-5}	0.0006	500×10^{-5}	0.040	850×10^{-5}	0.069
0.56×10^{-8}	0	87×10^{-5}	0.0013	105×10^{-5}	0.026	286×10^{-5}	0.070	329×10^{-5}	0.081
1.13×10^{-8}	0	49×10^{-5}	0.024	75×10^{-5}	0.037	133×10^{-5}	0.065	139×10^{-5}	0.068
2.25×10^{-8}	0	18×10^{-5}	0.0175	30×10^{-5}	0.029	36×10^{-5}	0.035	37×10^{-5}	0.036
4.13×10^{-8}	0	159.3×10^{-5}	0.063	217.4×10^{-5}	0.092	955×10^{-5}	0.210	1355×10^{-5}	0.254

¹ D, in this table = 1/4 in Table II.

If we assume that the fully developed grains in Svedberg's work were of about the same size as the undeveloped grains (some previous observations by one of us on the size ratio of developed to undeveloped grains using a developer similar to that of Svedberg substantiate this assumption), then the density values calculated from Svedberg's data on this basis, give D-log E values very close to those of the latter, as shown by comparison of Fig. 8 and Table IV with Fig. 6 and Table III above.

Our calculations are based on the mean projective areas given by S v e d b e r g. The maximum and minimum values of his four classes, particularly the larger sizes which are the most important, are quite wide apart so that the agreement just shown is all the more striking.

Svedberg's work on solarization and hydrogen peroxide action in this connection need not be discussed at present.

We reproduce here the size-frequency distribution curve (Fig. 9) plotted from Svedberg's data; this curve of course does not include fog grains.

Fig. 9

Our work which was commenced before the papers of Slade and Higson, and of Svedberg, appeared, has as its object the investigation of the relation of grain, in the statistical sense, or of dispersity, to the sensitometric properties of emulsions. This requires methods of assay and determination of the size frequency curves. A discussion of the methods already developed in this direction by ourselves and others will be published shortly.
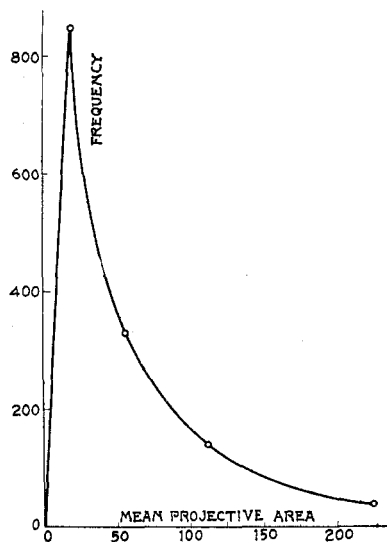
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