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DEPARTMENT OF THE ARMY  
Fort Detrick  
Frederick, Maryland

## SOME OPTICAL PROPERTIES OF TURBID MEDIA

Annales de Physique

Charles Chéneveau  
René Audubert

I. - Much research has been carried out on turbid media and in particular on their optical properties. The importance of the subject is certainly great since it encompasses colloidal solutions, emulsions, inclusions, precipitates, etc. Every law that can connect a physical property of a turbid medium with its constitution may therefore permit in practice the analysis of particles of which it is composed and, for example, may be applied to the determination of bacteria in biology as well as to the analysis of certain substances in chemistry.

First of all, can one define a turbid medium in a simple manner? We think that this is impossible, if we consider the optical properties which enable us to differentiate right away between a turbid and a transparent solution.

Certainly, a turbid medium is constituted in general of particles suspended in an intergranular medium, but these particles may be either opaque or transparent. In the latter case if the index of refraction of the transparent particles is equal to the index of refraction of the intergranular medium the medium will appear transparent: that is almost exactly so for suspensions of resins resulting from solutions of certain rubbers in benzene. If the refractive indices of the particular and interparticular medium are different the medium appears turbid; this is the behavior of oil in water, water in oil, of suspensions of resins (mastic, gamboge) in water containing a slight amount of alcohol, inclusions of liquids in resins etc.

A concept of a turbid medium therefore does not only imply the fact that there are solid or liquid particles suspended in an intergranular liquid or solid but also that the refraction of the media plays an important role.

On the other hand it is certain that the dimensions of the particles and their number also have their influence. From this point of view one

seems in general to have paid more attention to the first quantity than to the second, and nevertheless we seem intuitively to have always thought that the dimension and the number of particles are intimately connected with their effect, and that therefore it was rather their volume which affects their optical properties.

The optical properties - diffusion or absorption and polarization - have been studied almost exclusively in turbid media with opaque particles. The celebrated theory of Lord Raleigh<sup>1</sup> on the blue color of the sky - developed on the assumption that light is diffracted on particles which are small compared to the incident wave length, leads to the following formula where the thickness of the traversed medium is unity:

$$(1) \quad \frac{I}{I_0} = e^{-\frac{KNd^6}{\lambda}}$$

Here N is the number of particles of diameter  $d$  per unit volume,  $I_0$  the intensity of the incident light of wave length  $\lambda$ ,  $I$  the intensity of the transmitted light and K a coefficient which depends on the optical properties of the particle and of the intergranular medium. This formula has been verified many times on emulsions of mastic (Cap. Abney)<sup>2</sup>, on fine precipitates of silver chloride (Hyron<sup>3</sup> and Boutaric<sup>4</sup>) and also on the atmosphere itself (Crova<sup>5</sup>, Pertner<sup>6</sup> and Ehrenhaft<sup>7</sup>) have extended the experimental application to colloidal solutions. These different investigations have led to the result that in the case of particles whose diameter is very small compared to the wave length the exponent of the second factor in Lord Raleigh's formula is equal to 4. In many other cases, for example precipitation of silver chloride, it has this value only at the moment of formation of the precipitate; this is because of the variation of the size of the particles constituting the latter. Boutaric in particular has studied this phenomenon and was led to replace Lord Raleigh's formula by the following more general one:

$$(2) \quad \frac{I}{I_0} = e^{-\frac{kx}{\lambda^n}}$$

<sup>1</sup> Lord Rayleigh, Phil. Mag., 1871, 1881, 1899.

<sup>2</sup> Phil. Mag., Feb. 1871.

<sup>3</sup> C. R., Vol. 152, p. 143

<sup>4</sup> Thèse de Doctoral (Doctoral Thesis), Paris, 1918.

<sup>5</sup> Ann. Chim. Phys. (Annals of Chemistry and Physics), 6th Series, Vol. 20, 1890, p. 480; Vol 25, 1892, p. 534.

<sup>6</sup> Acad. Sciences de Vienne (Vienna Academy of Science), Vol. 73, 1901.

<sup>7</sup> Phys. Zeit (Journal of Physics), 5, 1904, p. 387.

where  $x$  is the thickness traversed.

He studied the variation of  $n$  from the moment of formation of the precipitate (AgCl). In his experiments  $n$  varied from + 4 at the initial moment to + 2 at the end of 60 minutes approximately. These limits are rather narrow and make one think that the corresponding increases in the diameter of the particles are small. However other authors (Keen and Porter)<sup>1</sup> have found without emphasizing it, variations of  $n$  which are much greater when studying the absorption of light through sulfur precipitated from sodium hyposulfite by acid; they observed that such a medium at first absorbed violet very strongly, and after a certain time it absorbs red preferentially.

In applying these results in formula 2 we see that  $n$  can therefore be both positive and negative.

II. However none of these publications mentions the close correlation between the diameter and the variation of  $n$ , as well as the effect of the number of particles with identical diameters. Thus it seemed of interest to see what would happen to Lord Raleigh's formula when applied to particles whose dimensions are equal to or greater than the wave length of the incident light. In this manner we have been led to investigate the optical properties of such media and to the systematic study of the effect of various factors, the diameter of the particles and their number per unit volume.

To this effect we used emulsions of gamboge and mastic obtained by precipitation of alcoholic solutions of these resins with water.

Such emulsions have a rather great stability and consist of particles which one can consider spherical and transparent. The mastic particles however differ slightly from those of gamboge:

The former are rather fragile and are crushed by pressure under the cover slide while the latter behave like true glass balls and break into pieces during the same operation. Furthermore there is an essential difference: the mastic is colorless while gamboge has a beautiful yellow coloration. We have also carried out measurements on fine silver chloride precipitates, on barium sulfate and on emulsions of oil in water and water in oil<sup>2</sup> and on liquid spherical inclusions in solid resins prepared by a

<sup>1</sup>Proc. Roy. Society, Vol. 89, 1914, p. 340.

<sup>2</sup>One can obtain rather easily a relatively stable emulsion of water in oil by shaking the oil with lime water; the opposite, a suspension of oil in water is obtained by emulsification in a sodium hydroxide solution. The reason for the success of these two procedures is probably the difference of the surface tension of the calcium and sodium hydroxide soap films that are formed.

procedure which one of us has discovered. Let us note in passing that though the stability of these inclusions is much greater than that of gamboge and resin emulsions, we have been unable to obtain a turbid medium which is stable indefinitely.

III. We shall restrict our description to the investigation of the absorption and diffusion carried out on such media; because of the dimensions of the particles, their polarization is negligible, though not equal to zero.

#### Preparation of the Emulsions.

In order to determine the effect of the number of particles per unit volume and of their diameter we have prepared, following the fractionated centrifugation technique described by Jean Perrin<sup>1</sup> an entire series of homogenous emulsions of mastic and gamboge comprising diameters ranging from 1 to 12  $\mu$  and concentrations ranging from  $10^6$  to  $5 \times 10^3$  particles per cc. Even though the procedure for preparing large particles permits the preparation of particles with a diameter of 50  $\mu$  we could in our experiments only use particles with a diameter smaller than 12  $\mu$ ; because above this value the spheres have inclusions or are covered by much smaller particles and this modifies their optical properties. Furthermore, measurements were difficult because of the very sizable sedimentation which occurred.

#### Measurements of N and d.

The evaluation of the parameters N and d has been carried out by a very large number of microscopic measurements (for the diameters the Perrin alignment method was used, for the concentrations a method similar to hematimetric ones). The calculated precision is 3% on the average.

#### Absorption Measurement.

These measurements were carried out with Fery's spectrophotometer<sup>2</sup>. In order to eliminate the visual error, due to the defects of the eye (Broca)<sup>3</sup> which is large when compared to the rest, we have taken a great number of measurements on the same emulsion; the measurements check each other. In this manner we have determined by a series of experiments the deviation of our measurements which is about 4 to 5%.

As a check on this precision we have used the verification of the classical exponential law which relates the transmitted intensity to the

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<sup>1</sup>Les Atomes (The Atoms), 1913.

<sup>2</sup>Journ. Phys. (Journal of Physics), Vol. 9, 4th Series, 1910, p. 819.

<sup>3</sup>Physique Biologique (Biophysics), Vol. 2: Photometry.

thickness of the traversed medium.

In order not to introduce large constants into our equations we have been obliged to use as unit of length the  $\mu$  ( $10^{-4}$  cm) and as unit of volume the cubic  $\mu$  ( $10^{-12}$  cm<sup>3</sup>).

#### IV. EXPERIMENTAL RESULTS - 1. Absorption

We have measured the absorption of the different emulsion series, prepared as described above, in order to find out whether the numerical results show the simple relation between the ratio  $\frac{I}{I_0}$  of the transmitted

light to the incident light and the parameters  $N$  and  $d$  which have already been defined.

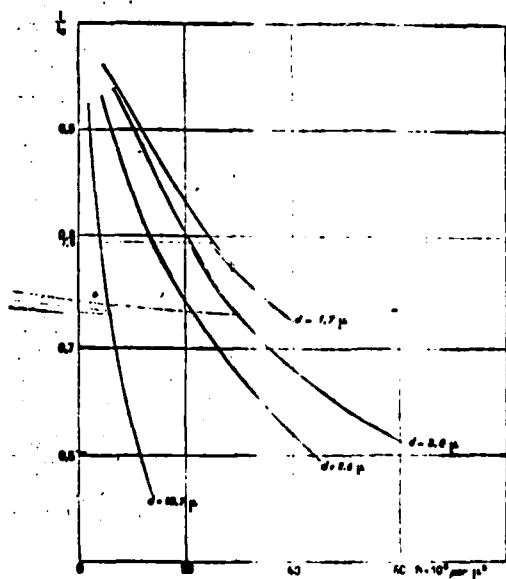


Figure 1.

We have shown our results graphically (curves) plotting the ratio  $\frac{I}{I_0}$  on the ordinate and either  $N$  or  $d$  on the abscissa. In both cases the transmission coefficient is a continuous function of the variable under consideration. But since these curves did not always fall into order of increasing value of  $N$  or of  $d$  (Fig. 1) we had the idea of considering the product  $Nd$  as an independent variable. This product represents, except for a constant factor, the total volume of the particles or their total mass.

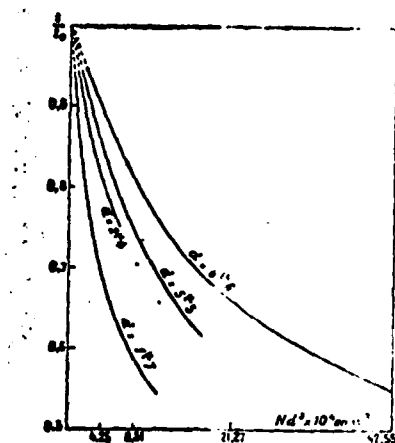


Figure 2.

The previously noted anomaly disappears as is shown in Figure 2.

The function  $\frac{I}{I_0} = f(Nd^3)$  can easily be determined; as a matter of fact if one plots the values of  $\log(Nd^3)$  on the abscissa and the corresponding values of  $\log \left[ \bar{\log} \left( 1 - \frac{I}{I_0} \right) \right]$  on the ordinate the points obtained graphically fall essentially along straight lines whose equation is:

$$(3) \quad \log \left[ \bar{\log} \left( 1 - \frac{I}{I_0} \right) \right] = \log K - \alpha \log Nd^3.$$



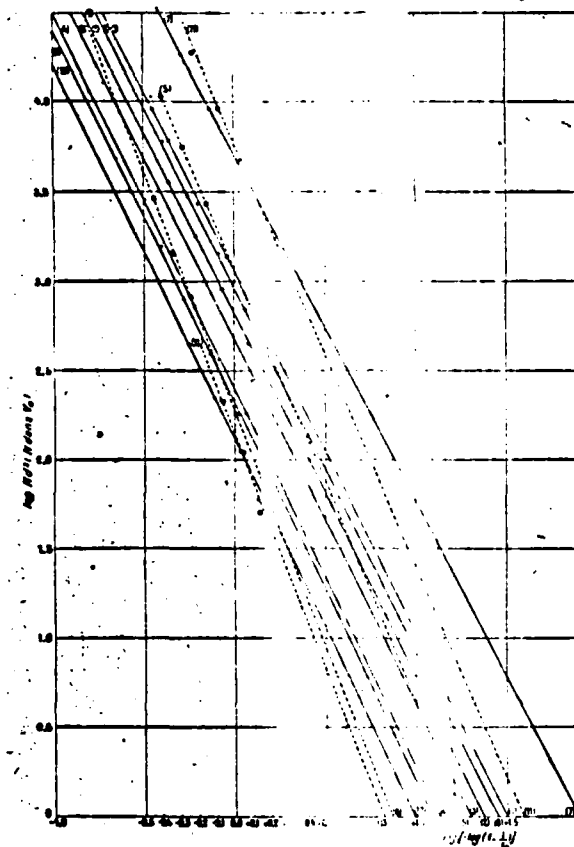


Figure 3.

It is interesting to note that the slopes of the straight lines obtained for a given wave length are the same regardless of the diameter or the nature of the particle (Fig. 3); on the other hand the ordinate at the origin ( $\log K$ ) is related to the diameter by the equation:

$$\log K = \log A + \beta \log d$$

in which  $A$  and  $\beta$  are variable coefficients. The first,  $A$ , varies with the wave length and the nature of the particle and the second  $\beta$  varies with the nature of the particle only.

Consequently all these results can be summarized in the following equation which expresses the relation between the absorption  $1 - \frac{I}{I_0}$  of the

emulsion and its physical properties:

$$(4) \quad 1 - \frac{I}{I_0} = e^{-\frac{Ad\beta}{(Nd^3)^\alpha}}$$

The measured values of  $\frac{I}{I_0}$  are listed in the summary table given at the end of the paper. The following table gives, for two wave lengths the value of the coefficients of equation (4) for mastic and gamboge.

	$\alpha$		$\beta$	$A$	
	$\lambda = 0.644\mu$	$\lambda = 0.498\mu$		$\lambda = 0.644\mu$	$\lambda = 0.498\mu$
Mastic	0.5	0.4	0.5	$1.8 \cdot 10^{-6}$	$1.0 \cdot 10^{-2}$
Gamboge	0.5	0.4	1.0	1.1 "	0.6 "

Within the experimental error the values calculated by the above equation, valid only for particles whose diameter is greater than the wave length, are identical with observed values. Random examples are:

	for $\lambda = 0.644\mu$	$I/I_0$ calculated	$I/I_0$ observed	approximation
Mastic	No. 16	0.93	0.93	0 0/0
	No. 2	0.66	0.64	3 --
	No. 1	0.57	0.56	2 --
Gamboge	No. 15	0.94	0.91	3 0/0
	No. 5	0.72	0.70	3 --
	No. 1	0.55	0.56	2 --

The extinction coefficients found for mastic are always smaller than those found for gamboge; this difference is of the order of 0.14 and is independent of the number and size of the particles. It characterizes probably the absorption due to the coloration of gamboge.

Example for 0.644 $\mu$ :

	$d$	$Nd^3$	$I/I_0$		Difference
Mastic	1.7 $\mu$	400	0.84	0.70	0.14
Gamboge		600	0.77	0.64	0.13
Mastic	2.5 $\mu$	600	0.72	0.58	0.14
Gamboge		1.000	0.80	0.66	0.14
		1.600	0.88	0.75	0.13

Equation 4 obtained experimentally does not show the effect of the wave length, while Lord Rayleigh's equation, which applies to all small particles involves the variable  $\lambda$  explicitly. Expression (1) cannot be applied to particles whose dimensions are large compared to the wave length of the incident light. But perhaps with some modifications it could be made applicable to large particles. With this in view by replacing it by the much more general equation given by Boutaric<sup>1</sup>)

$$(5) \quad \frac{I}{I_0} = e^{-\frac{A}{\lambda d}}$$

A, being a certain function of N, of  $d$  and of the optical properties of the particles and of the interparticle medium, experience has shown that by plotting the values of  $\log \lambda$  on the abscissa and the corresponding values of  $\log \left[ 1 - \log \left( 1 - \frac{I}{I_0} \right) \right]$  one obtains straight lines of the form:

$$\log \left[ 1 - \log \left( 1 - \frac{I}{I_0} \right) \right] = \log A + n \log \lambda.$$

These results indicate that it is justifiable to use equation (5) for large particles and that the exponent n is independent of the wave length. This has been confirmed by a very large number of measurements carried out on inclusions, precipitates and emulsions of oil in water and water in oil.

On the other hand, within our limits we found that the function A is of the form:

<sup>1</sup> Loc. cit., p. 83.

$$A = KNd$$

K being a coefficient depending solely on the optical properties of the particles and of the interparticle medium. Assuming that this proportionality factor is identical with that of Lord Rayleigh's equation

$$\frac{8\pi^3}{3} \left(\frac{D' - D}{D}\right)^2$$

we find, by equating it to the numerical value obtained for K per unit of thickness traversed:  $\frac{D'}{D} = 0.09$  approximately; it is interesting to note that this value is precisely that of the ratio

$$\frac{N^2 - N_0^2}{N^2 + 2N_0^2},$$

where N (Approximately 1.48) and  $N_0$  (approximately 1.33) represent the refractive indices of the particles and of the interparticle medium.

The absorption can thus be given by the equation:

$$(6) \quad 1 - \frac{I}{I_0} = e^{-\frac{KNd}{\lambda^n}}$$

## 2. Dispersion by Internal Diffusion.

This last equation (6) is superior because it definitely shows the variation of the absorption with different radiations.

Thus when measuring the intensities  $I'$  and  $I''$  transmitted by two wave lengths  $\lambda'$  and  $\lambda''$  one finds, since  $\underline{n}$  is independent of the wave length:

$$\underline{n} = \frac{\log \left(-\log \frac{I'}{I_0}\right) - \log \left(-\log \frac{I''}{I_0}\right)}{\log \lambda' - \log \lambda''}.$$

We have determined the values of  $\underline{n}$  for a series of homogeneous emulsions with different concentrations and diameters; the results are listed in the summary table.

From this table it is apparent that  $\underline{n}$  depends both on N and  $\underline{d}$ ; one could, a priori, predict the effect of the diameter but not that of the number of particles per unit of volume. This fact has, to the best of our knowledge, never been noted before. This systematic study however shows that the laws which govern variation with N and  $\underline{d}$  are analogous:

1. For each diameter, the curves  $n = f(N)$  (Fig. 4) show a minimum which is especially marked for the large diameters and whose position moves away from the origin with decreasing diameter.

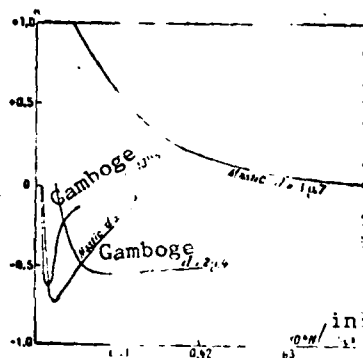


Figure 4

Within the limits of the experiment the variation of  $\underline{n}$  for small diameters and high concentrations can be represented by the relation  $n = A + B \log N$ .

2. The curves  $n = \phi(d)$  (Fig. 5) also have minima which move away from the origin with decreasing  $N$ ; furthermore the magnitude of these minima decreases with the concentration. The extrapolations of the curves to the y-intercept seem to converge to a point for  $n = 4$  for  $d$  approaching zero. This result confirms the law of Lord Raleigh for small particles. This extrapolation could not be carried out with enough precision for the curves  $n = f(N)$ .



Figure 5

3. All these results indicate that  $\underline{n}$  is a continuous function of the two variables  $N$  and  $\underline{d}$ , and can have, as is shown in the above figures (4) and (5) all the possible positive and negative values between an upper limit, which is probably 4, and a lower limit, which in our experiments never went below -1.

When  $\underline{n}$  is positive the medium is more absorbent for the small wave lengths; the opposite happens when  $\underline{n}$  is negative, red is dispersed more. In particular, at a constant diameter the dispersion of the medium depends only on the number of particles and  $\underline{n}$  can pass from a negative value to a positive one when  $N$  decreases. We have obtained very clear-cut results with gamboge and mastic suspensions with a diameter in the vicinity of  $1.7 \mu$ . For the former when  $N$  varies between  $4 \times 10^7$  and  $5 \times 10^8$  per cc,  $\underline{n}_B$  passes from 0.75 to + 0.70; for the latter when  $N$  varies between  $2.5 \times 10^7$  and  $1.6 \times 10^8$  per cc,  $\underline{n}$  passes from -0.51 to + 1.0.

Incidentally it is interesting to note that one can make a new verification of Lord Raleigh's law for small particles by plotting the values of  $I/I_0$  on the abscissa and the corresponding values of  $\underline{n}$  on the ordinate.

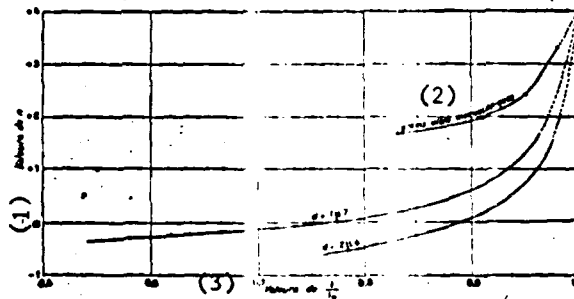


Figure 6.

Legend: 1. Value of  $\underline{n}$   
 2. Ultra-microscopic grains  
 3. Values of  $I/I_0$

One then obtains curves (Fig. 6) whose shape is similar to the previous ones. Some have a minimum and all the extrapolations seem to pass through the point  $\underline{n} = 4$ .

5. Calculations can determine the shape of the function  $\underline{n} = \phi(N, \underline{d})$ . By referring to equations (4) and (6) previously established for the absorption in turbid media of large particles one gets by equating them:

$$1 - e^{-\frac{KNd}{\lambda^n}} = e^{-\frac{Ad^\beta}{(Nd^3)^\alpha}}$$

Then by expanding the first member in a series to the second term

$$\frac{KNd}{\lambda^n} = e^{-\frac{Ad^\beta}{(Nd^3)^\alpha}}$$

and by taking natural logarithms:

$$(7) \quad n = \frac{1}{\log_e \lambda} \left[ \log_e K + \log_e N + \log_e d + \frac{Ad^\beta}{(Nd^3)^\alpha} \right]$$

When one takes the second derivative of  $\underline{n}$  with respect to  $N$  for instance one obtains the value

$$\frac{d^2 n}{dN^2} = -\frac{\alpha}{N_1^2 \log_e \lambda},$$

$N_1$  being the value for which the derivative  $dN/dN$  becomes equal to zero, e.g.  $N_1 = (\alpha Ad^\beta - 3\alpha^2)^{1/\alpha}$ . Since  $\alpha$  and  $N_1^2$  are positive and since  $\log \lambda$  is always negative  $d^2 n/dN^2$  is always less than 0. The value  $N_1$  thus corresponds to a minimum for  $\underline{n}$ . In view of the symmetry of the equation a similar course of reasoning would indicate a minimum for  $\underline{n}$  when  $\underline{d}$  would be considered as a variable. Experiments have borne out this manner of reasoning. By replacing, in equation (7), the various constants by their experimental values and by calculating  $\underline{n}$  one finds values agreeing with observation within the experimental errors. The same applies to the value of the minimum and to the corresponding  $N_1$ .

Equation (7) also indicates that the minima of the curves obtained when either  $N$  or  $d$  is considered as variable are less marked when  $d$  or  $N$  are smaller. Finally one finds again the logarithmic law obtained experimentally for media with small particles and high concentrations, because the last term can be neglected.

V. Turbid Non-Homogeneous Media. Up to now we have limited ourselves to the investigation of the absorption and the dispersion observed in media of particles with the same diameter.

Equation (4) established experimentally for these homogeneous media could, a priori, permit one to predict the extension of the results so acquired to turbid media constituted of particles with different diameters. Experiments have confirmed this hypothesis.





Garnett<sup>1</sup> has already found in colloidal metal solutions this influence of mass on the absorbing properties of turbid media. Very recently O. Bloch and F. F. Renwick<sup>2</sup>, while studying the surface opaqueness of the silver emulsions of photographic plates, found empirically a logarithmic law between the absorption and the mass which is similar to the equation which we found. More recently M. F. Vlès<sup>3</sup> while searching for an optical determination for bacterial broth found a simple analytical equation given by a hyperbolic relation between the absorption and the total mass of the bacteria.

Because of the very diverse conditions under which these investigations have been carried out it is possible that the various forms of the mass law which were found in each case are true within the experimental conditions. However it is also true that there is a very general, simple relation between the absorption and the total mass of a suspended substance which produces the optical turbidity.

In as far as our work is concerned, we think that the exponential law, which we found, is that which fits best when one works with particles whose diameter varies between 1 and 12  $\mu$ . We can even add that this law still applies to particles whose diameter is smaller than 1  $\mu$ . We have carried out determinations on ultramicroscopic particles which do not centrifuge down and whose diameter was of the order of 0.1  $\mu$  and we have again found the exponential mass law.

2. For dispersions by internal diffusion we have found for heterogeneous media again the same results obtained for homogeneous emulsions:  $\bar{n}$  is a function of both N and d, and the curves, drawn when N and d are considered as variables one at a time, have the same shape as those corresponding to emulsions with graded particles. As in the case of the latter they seem to converge at the point  $\bar{n} = 4$ , when d approaches zero. Also  $\bar{n}$  can assume both positive and negative values, depending on the case.

Furthermore, for high concentrations and a mixture of particles with medium and small diameters we have found again the logarithmic law  $\bar{n} = A + B \log N$ . These results have been confirmed by a great number of determinations on very diverse media such as: suspensions of fine precipitates of silver chloride, barium sulfate and chromate, emulsions of oil in water and water in oil and emulsions of gamboge and mastic.

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<sup>1</sup>Garnett, Phil. Trans. (A) 203, 1904, p. 205 and 385, 1906, p. 237. For this subject matter it would be useful to refer to the work of E. F.

<sup>2</sup>Burton: The Physical Properties of Colloidal Solutions, 1916.

<sup>3</sup>The Photographic Journal, Vol. 61, 1916, p. 49.

C. R., Vol. 78, p. 575 and 794.

## VI. General Conclusions.

1. The diffusion of light by turbid media involves diffraction if the particles have a diameter smaller than the wave length of the incident light; but the interpretation, by diffraction, of the optical phenomena obtained with large particles is insufficient because, as we have seen, Lord Raleigh's equation cannot be used in its true form. Probably all the optical phenomena - diffraction, refraction, reflexion - must be taken into consideration to explain the experimental facts which have been discussed. The general theory of these phenomena must be very complex; it has been touched upon in various forms by different physicists (Garnett, Mie etc.)<sup>1</sup> for metallic colloidal solutions; in this very special case the electromagnetic theory of light suggests calculations which partly explain the experimental facts but which cannot be applied to non-conductive particles - which is the case of those media which we have investigated. We have thus restricted ourselves to look among the pertinent physical phenomena for the one whose role is most important.

Since the effect of diffraction is negligible for reasons explained earlier in this paper we have first attempted to explain the results of our investigation by refraction. A reasoning similar to that used for the basic theory of the rainbow has shown that this phenomenon considered by itself is insufficient. Likewise, one cannot apply to these media the theory of Christiansen's<sup>2</sup> experiments. Reflexion by itself seems to be the phenomenon whose effect is preponderant. Starting with this hypothesis a simple course of reasoning can as a matter of fact yield calculated values of the index of the medium which are identical with experimental ones.

Let us imagine a turbid medium in which the transparent particles are uniformly distributed. Let us consider, within a thickness  $e$  of this medium, a row of particles with diameter  $d$ , are separated by intervals  $d'$  and are placed in the course of a beam of monochromatic light. Let  $N'$  stand for the index of refraction of the interparticular medium. Let us calculate the delay in the propagation of light between ray 2 which traverses the interparticular medium and neighboring ray 1 which successively encounters the row of particles along their axis (see Fig. 7).

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<sup>1</sup> c.f. the book by E. F. Burton. The Physical Properties of Colloidal Solutions (loc. cit.).

<sup>2</sup> Ann. der Phys. (Annals of Physics), November 1884.

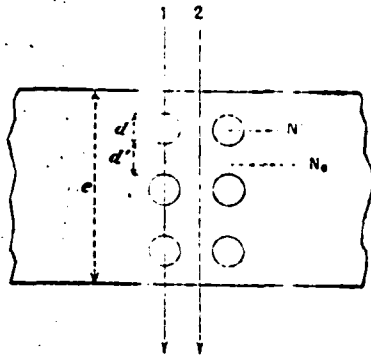


Figure 7

Let us designate the index of the turbid medium by  $N$  and let us assume that the velocity undergoes, at each surface of separation a loss of  $\pm a$  percent according to whether the index  $N'$  is greater or smaller than  $N_0$ ; if the row consists of  $p$  particles and  $p + 1$  intervals one has:

$$(N - N_0)e = N'd \left( \frac{1}{1 \pm a} - \frac{1}{1 \pm 3a} + \dots + \frac{1}{1 \pm (2p - 1)a} \right)$$

$$-pdN_0 + N_0d' \left( \frac{1}{1 + 2a} + \frac{1}{1 + 4a} + \dots + \frac{1}{1 + 2pa} \right) - pd'N_0$$

From which one can deduce:

$$(9) \quad (N - N_0)e = pd(N' - N_0) \pm pa \sqrt{pdN' - (p + 1)d'N_0}$$

From this result one can draw the following conclusions:

1. If  $d$  is small compared with  $d'$ , equation (1) resolves into

$$(N - N_0)e = \mp p(p + 1)ad'N_0.$$

If one assumes that the loss  $a$  is due only to the reflexion and that the value of  $a$  is

$$= \frac{N_0 - N'}{N_0 + N'}$$

one can evaluate the value of  $(N - N_0)$  for different cases and compare it with the value obtained experimentally by the method of total reflection.

We have carried out these determinations with the Pulfrich reflectometer for the D line of sodium, and checking with white light for inclusions by the microscopic method of the Duc de Chaulnes. One can conclude from the figures of the subsequent table that agreement between the equation and experimental results is satisfactory.

	$N - N_0$	
	Calculated	Observed
Inclusion of water $N' = 1.33$ in a resin $N_0 = 1.48$	0.16	0.16-
Emulsion of water $N' = 1.33$ in oil $N_0 = 1.47$	0.08	0.08+
Emulsion of oil $N' = 1.47$ in water $N_0 = 1.33$	0.07	0.07

Here the index of the turbid medium is always greater than that of the interparticular medium.

It seems justifiable to assume that reflection plays an important role in all optical phenomena concerned with media with large particles.

2. If  $N' = N_0$ ,  $a = 0$  and the second term of equation (9) becomes, like the first, equal to zero. It is easy to see that in this case the transparent particles in suspension in a medium with the same index of refraction will not give rise to any optical turbidity. This fact is confirmed experimentally as we have shown above for suspensions of resins made by dissolving certain types of rubber in benzene.

In the last account these experiments explain only incompletely the optical phenomena observed in turbid media with large particles. Even though they show the reason for the variation of the index they cannot be used to determine the dispersion mechanism. It is thus justified to assume that all the optical phenomena that one can consider must participate; the magnitude of each contribution depends on the physical properties of the particle.

One can correlate the phenomena which we have just described with those observed for media with smaller particles. If one represents the intensity of the light transmitted by a turbid medium by the equation:

$$\frac{I}{I_0} = e^{-\frac{A}{\lambda^n}}$$

where  $A$  and  $n$  are a function of  $N$  and  $d$ , it is easy to see, by referring to the results obtained successively by Abney, Hurion, Crova, Boutaric and

Vlès that one can arrange the values obtained for  $\underline{n}$  in the following order according to the dimensions of the particle:

Abney, Hurion, Crova and Boutaric	Atmosphere Fine precipitates at the beginning of their formation	n close to 4
Vlès	Bacteria	n between + 3 and + 2
Chéneveau and Audubert	Large transparent particles	n between + 4 and - 1

One could perhaps classify water among the substances, assigning the value of 4 to  $\underline{n}$ . The dispersion of light on its molecules would then be the explanation of the blue color when observed in rather great thickness.

As for the function  $\underline{A}$ , its upper limit is proportional to  $Nd^6$  and its lower limit, as shown by our experiments, is proportional to  $Nd$ .

Let us note here, in connection with the value of  $\underline{n}$  for the atmosphere, that certain investigators have found a value of  $n$  greater than 4.<sup>1</sup>

Boutaric has thought that this excess over the limiting value anticipated by Lord Raleigh's equation can be explained in terms of the fluorescence of the atmosphere. In order to test this hypothesis we have made measurements of  $\underline{n}$  in emulsions of gamboge and mastic containing traces of the fluorescent substances fluorescein and eosin. Up to a certain limit, which corresponds to the appearance of absorption bands, addition of fluorescein or eosin always increases the value of  $n$  to a considerable extent.

Examples:

	Initial emulsion	Emulsion plus
gamboge	n = 2	fluorescein n = 4.7
	n = 0.6	fluorescein n = 2.5
mastic	1.0	" n = 3.7
	2.1	" n = 4.8
	n = 2.0	eosin n = 5.3

<sup>1</sup>Boutaric, loc. cit.

The fluorescence of the solution can thus explain that  $n$  is greater than 4; but this effect appears to be limited by the appearance<sup>1</sup> of absorption bands or by the optimum fluorescence noted by Jean Perrin.

### 3. Applications.

From a practical point of view the optical properties which we have just described can be used immediately for the quantitative determination of suspensions. We have just seen that for heterogeneous turbid media (fine precipitates, gamboge emulsions, emulsions of mastic or oil etc.) the mass  $M$  is related with the ratio  $I/I_0$  by a relationship of simple exponential form:

$$\frac{I}{I_0} = 1 - e^{-\frac{B}{M^\beta}}$$

Measurement of  $I/I_0$  of a given medium can thus be used to obtain the total mass of the particles which constitute this medium, or, which means the same thing, the titer of the solution. This determination can be used each time one deals with a medium which does not sediment too rapidly. It will suffice to calculate, by means of two preliminary determinations on known concentrations, the constants  $B$  and  $\beta$  of the exponential equation. One can also obtain the mass  $M$  without resorting to calculation by equation; as a matter of fact it will suffice, once  $B$  and  $\beta$  are known, to construct a standard curve of the values of  $I/I_0$  for the known concentrations of the given medium. In order to obtain the concentration  $x$  of an emulsion of the same constitution it will be enough to measure  $I/I_0$  and to refer to the standard curve.

This last procedure seems to be the best way to proceed because, even in cases where the exponential equation would not exactly apply to media other than those investigated as has been found by Vlès<sup>2</sup> for bacteria for instance - it is still possible to determine the titer by knowing  $I/I_0$ .

Actually in all cases the ratio  $I/I_0$  must be a contiguous function of  $M$ . Various investigators, including Richards and Wilson<sup>3</sup> have attempted to evaluate the difference in the concentrations of the two suspensions by comparing the intensity of the light they diffuse with one another. We think that these methods, referred to as nephelometric - are inaccurate

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<sup>1</sup>Ann. de Phys., Vol. 10, 1918, p. 133.

<sup>2</sup>Vlès, loc. cit.

<sup>3</sup>Amer. Chem. Journal, Vol. 31, 1904, p. 235.

except in the case of suspensions of very fine particles ( $n = 4$ ) because of the variations which the exponent  $n$  of the wave length undergoes as a function of the concentration. On the other hand the determination of  $I/I_0$  yields exact results. Furthermore the sensitivity with which the determination of the titer can be carried out is very good as is shown in the following examples:

	Thickness of cell: 4 cm					
Mastic (g/liter)	M	0.060	0.041	0.0306	0.0206	0.0150
	$\frac{I}{I_0}$	0.677	0.748	0.810	0.860	0.900
	Thickness of cell: 8 cm					
AgCl (g/liter)	M	0.055	0.0354	0.0177	0.0088	
	$\frac{I}{I_0}$	0.578	0.677	0.804	0.884	

These numbers indicate that in the case of silver chloride we could measure differences of the order of 0.001 g/liter with an accuracy of 2%; and in the case of mastic we could evaluate differences of the order of 0.0008 with an accuracy of 1%.

Vlès, de Wattevil and Lambert<sup>1</sup> have designed an opacimeter which can be used to determine emulsions of microbes.

It is interesting to note, in view of the complete agreement of the results indicates that the individual shape of the particles only enters in a secondary fashion.

In addition to the very many services that a method of this type can give when applied to chemical determinations we think that it would also be of interest for certain physicochemical speculations. It could for instance resolve a certain number of problems concerned with the process of formation of precipitates and their reaction velocity.

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<sup>1</sup>C. R., Vol. 168, 1919, p. 797.

Summary table

Gamboge				Mastic			
No of order	$N \times 10^6$ per $\mu$	$\frac{I}{I_0}$	n	No of Order	$N \times 10^6$ per $\mu$	$\frac{I}{I_0}$	n
		$\lambda=0.644\mu$	$\lambda=0.498\mu$			$\lambda=0.644\mu$	$\lambda=0.498\mu$
d = 10.7 $\mu$	1	0.564	0.578	--	28.0	--	-0.10
	5	0.695	0.715	1	14.0	0.562	-0.44
	9	0.813	0.839	5	7.0	0.645	-0.66
	13	0.921	0.924	9	3.5	0.764	-0.61
d = 3.5 $\mu$	2	0.612	0.649	13	1.7	0.882	-0.10
	6	0.727	0.757	2	9.4	0.637	-0.65
	10	0.850	0.862	6	4.7	0.764	-0.
	17	--	--	10	2.3	0.856	-0.20
	14	0.932	0.932	14	1.1	0.936	0
	3	0.599	0.639	3	31.1	0.812	-0.40
d = 2.5 $\mu$	7	0.712	0.741	7	15.5	0.907	+0.25
	11	0.820	0.842	11	7.7	0.943	+0.74
	18	--	--	--	507.2	--	-0.54
	15	0.915	0.915	4	253.6	0.548	-0.50
d = 1.7 $\mu$	4	0.728	0.766	8	126.8	0.630	-0.12
	8	0.836	0.869	12	63.4	0.753	+0.07
	12	0.917	0.921	15	31.7	0.850	+0.30
	16	0.955	0.945	16	15.3	0.928	+1.00
Particles of approximate diameter							
156200	0.873	0.788	+2.3	169400	0.834	0.758	+1.7
78100	0.934	0.872	+2.8	89700	0.909	0.853	+2.0
39050	0.971	0.933	+3.3	49850	0.955	0.919	+2.4
19525	0.978	0.951	+3.8	24925	0.978	0.947	+3.5