

On the Transmission Colours of Sulphur Suspensions

C. V. Raman and Bidhubhusan Ray

Proc. R. Soc. Lond. A 1921 **100**, 102-109

doi: [10.1098/rspa.1921.0074](https://doi.org/10.1098/rspa.1921.0074)

Email alerting service

Receive free email alerts when new articles cite this article - sign up in the box at the top right-hand corner of the article or click [here](#)

REFERENCES.

- (1) Chaney, 'Trans. Amer. Electro-Chemical Soc.,' vol. 36 (1920).
- (2) Quoted by Dewar, 'Proc. Roy. Inst.,' vol. 18 (1906).
- (3) Harkins and Ewing, 'Proc. Nat. Acad. Sciences (U.S.A.),' vol. 6, p. 49 (1920)
- (4) Miller, 'Chem. Met. Eng.,' vol. 22, p. 949 (1920).
- (5) Williams, 'Roy. Soc. Proc.,' A, vol. 98, p. 223 (1920).
- (6) Titoff, 'Zeit. f. Physik. Chem.,' vol. 74, p. 641 (1910).
- (7) Baerwald, 'Ann. Physik,' vol. 23, p. 84 (1907).
- (8) Homfray, 'Zeit. f. Physik. Chem.,' vol. 74, p. 129 (1910).
- (9) Dewar, 'Proc. Roy. Inst.,' vol. 18, p. 433 (1906).
- (10) Baly and Donnan, 'Journ. Chem. Soc.,' vol. 81, p. 912 (1902).
- (11) Dewar, 'Roy. Soc. Proc.,' A, vol. 74, p. 122 (1904).
- (12) Williams, 'Proc. Roy. Soc. Edin.,' vol. 39, p. 48 (1919).
- (13) Lamb, Wilson, and Chaney, 'Journ. Indust. Eng. Chem.,' vol. 11, p. 423 (1919).
- (14) Philip, Dunnill, and Workman, 'Journ. Chem. Soc.,' vol. 107, p. 362 (1920).

On the Transmission Colours of Sulphur Suspensions.

By C. V. RAMAN, M.A., Palit Professor of Physics, and BIDHUBHUSAN RAY,
M.Sc., Lecturer in Optics, Calcutta University.

(Communicated by Dr. G. C. Simpson, F.R.S. Received June 8, 1921.)

1. *Introduction.*

In the 'Proceedings of the Royal Society,'* Keen and Porter described some interesting optical effects exhibited by suspensions of finely-divided sulphur, obtained by adding dilute sulphuric acid to a weak solution of sodium thiosulphate. As is well known, the solution (which is at first perfectly transparent) becomes turbid when the particles form in it, and the transmission of light by the suspension gradually diminishes in intensity. The colour of the transmitted light, which is at first white, also changes, becoming yellow, orange, red, and then deep crimson red. Finally, the solution (if in a sufficiently thick layer) becomes almost completely opaque. This had been previously supposed to terminate the sequence of phenomena. Keen and Porter observed, however, that after further lapse of time, light begins again to be transmitted by the suspension, the colour of the light which passes through being at first indigo, then blue, blue-green, greenish-yellow, and finally again white. This remarkable reappearance of the transmitted light was quantitatively studied by them, measurements being

* Ser. A, vol. 89, p. 370 (1914).

On the Transmission Colours of Sulphur Suspensions. 103

made of the intensity of the transmitted light in the various stages of the experiment, red and blue glass plates being used to approximately monochromatise the light of the source. Keen and Porter published curves showing the fraction of the incident light which is transmitted as a function of the time, and found that the shape of the curve is different for different parts of the spectrum, which is of course to be expected, in view of the colours exhibited by the solution when the incident light is white. The diameter of the sulphur particles was also found to increase with time. No attempt was, however, made to explain the observed phenomena on theoretical principles.

The problem was then taken up by the late Lord Rayleigh,* who attempted to investigate the effects on the basis of the mathematical theory of the scattering of light by small transparent spheres. The explanation of the phenomena observed in the earlier stages of the experiment presented no difficulty. As the particles grow in size, the suspension refuses to transmit, first the shorter waves, and then, finally, the whole visible spectrum. This is precisely what is to be expected, in view of the fact that the scattering power of the particles grows rapidly as their size in relation to their wave-length increases and the transmitting power of the suspension decreases *pari passu* with the increase in the proportion of the energy scattered. Lord Rayleigh did not, however, find it possible to explain the reappearance of the transmitted light in the later stages studied by Keen and Porter, and he went so far as to suggest that there might be some doubt whether the effect was really due to transmitted light in the technical sense of the term.

The present authors have thought it worth while, in view of Rayleigh's remarks, to repeat the experiments, and have obtained results confirming those of Keen and Porter. It is found that the suspension does, indeed, after a certain stage in the growth of the particles, begin again to transmit light regularly, in the strictest optical sense of the term. This is shown by the observation that the coloured light passing through is capable of forming sharply defined optical images. Further, as has already been remarked by Keen and Porter, the effects are not peculiar to sulphur suspensions, but have also been observed in other cases.† The phenomena are thus undoubtedly genuine, and demand an explanation.

It should be remarked, however, that there is a discrepancy between the dimensions of the particles as given by Keen and Porter, and as observed by

* 'Roy. Soc. Proc.,' A, vol. 90, p. 219 (1914).

† Abney, 'Phil. Trans.,' Part II, p. 653 (1880); W. Ritz, 'Comptes Rendus,' vol. 143, p. 167 (1906).

us at the different stages of the experiment. We find that, at the stage of minimum transparency, the diameters of the particles range from 0.7μ to 0.9μ , and, later, increase in the stage of reappearance of the transmitted light from 1.0μ to 1.3μ .*

It is proposed in the present paper to show how the phenomena described by Keen and Porter may be very simply and quantitatively explained on theoretical principles.

2. *The Theory of the Colours.*

The vanishing and subsequent reappearance of the transmitted light (shorter wave-lengths first, longer wave-lengths afterwards), with the increase in the size of the suspended particles, is seen to follow as a natural consequence of theory when we consider the manner in which the attenuation of the light in passing through a turbid medium occurs.

Consider the passage of a plane wave-front through a thin layer of the medium containing n scattering particles per unit volume. We may, following Rayleigh,† divide the wave-front into elementary areas, in accordance with the Fresnel-Huyghens principle, the effect of the secondary waves diverging from these elements at an external point, P, being integrated to find the amplitude and phase of the transmitted wave. In the present case an appreciable part of the area of the wave-front is occupied by the scattering particles, which are supposed to be sufficiently numerous and irregularly arranged. We have to consider this part separately from the rest of the wave-front. The attenuation of the light in passing through the medium is, according to this procedure, seen to be due to two causes:— (1) the decrease in the area, and consequently also of the resultant effect of the undisturbed portion of the wave-front; and (2) the interference with this of the light scattered in the direction of the primary wave by the particles lying in the wave-front.‡

In the case of the very finest particles, the effect contemplated in (1) is very small, and the phase of the scattered waves in relation to that of the

* The figures given by Keen and Porter are much larger and appear to be incorrect. The figures noted above represent the average size of the bulk of the particles, but there are many both smaller and larger.

† 'Scientific Papers,' vol. 4, p. 399.

‡ A question may be raised whether *multiply-scattered* light should not also be taken into account in this connection. In reference to this, it may be pointed out that the investigation given below does take this into account in so far as the effect of light reaching the given stratum in the direction of propagation after scattering by the layers *preceding* it is concerned, and this is the only portion of the multiply-scattered light which is in permanent phase-relation with the primary wave and need be taken into account for our present purpose.

On the Transmission Colours of Sulphur Suspensions. 105

primary waves is such that the interference effect referred to in (2) does not (to a first approximation) alter the amplitude of the resulting effect, but only affects its phase.* With increasing size of the particles, however, the case is altered. The effect (1) becomes considerable, and results in a continuous decrease in the transparency of the medium with increasing size of the particles, the number being assumed to be the same. The amplitude of the light scattered by individual particles also increases rapidly at the same time, and the importance of the effect (2) is therefore enhanced; but whether this results in an increase or decrease of the amplitude of the transmitted wave obviously depends on the phase relationship between the primary and scattered waves in the direction of regular propagation. If the phase of the scattered waves lags sufficiently behind that of the primary waves, we may have actually an increase in the resulting transmission of the light by the suspension with increased size of the particles. As we shall see presently, this is what actually happens.

In order to calculate the amplitude and phase of the secondary waves scattered in the direction of the primary wave, by the dielectric particles, we utilise the formulæ given by Prof. Love as corrected by Rayleigh.† For the case in which the refractive index of the particles is 1·5, the numerical values have been computed by Rayleigh, the ratio of the circumference of the particles to the wave-length having the series of values 1, 1·5, 1·75, 2, and 2·25. The relative refractive index of sulphur particles in water being 1·95/1·33 is sufficiently near to 1·5 for us to accept Rayleigh's numerical values as approximately applicable in the present case. From the Table given by Rayleigh it is seen that the amplitude of the scattered wave in the direction of the primary is independent of the plane of polarisation (as is of course to be expected *a priori*), and increases continually and rapidly with the size of the particles. For our purpose, we require also the numerical values for the case of much larger particles than those used in Lord Rayleigh's calculations. The numerical calculations are extremely tedious but have fortunately been already carried out by one of us (Bidhubhusan Ray) for a ratio circumference/wave-length = 5 in connection with an investigation (which is being separately published) "On the Colour and Polarisation of the Light Scattered by Sulphur Suspensions." Utilising this result in conjunction with the calculations of Rayleigh, the graphs in figs. 1 and 2 have been drawn

* In this case, the attenuation has been calculated by Rayleigh by an indirect method, depending on the determination of the energy of the waves scattered by individual particles. As to the validity of this process when the particles are larger in size, we shall have some remarks to offer later in the course of the paper.

† 'Roy. Soc. Proc.,' A, vol. 84, p. 30 (1910).

showing the amplitude and phase of the scattered waves as a function of the ratio circumference/wave-length for sulphur particles in water.

We are now in a position to write down the expression for the coefficient of transmission of light through the suspension. Assuming the amplitude of the primary vibration to be unity, the expression for the scattered disturbance due to a single particle in a direction nearly coinciding with $\theta = 180^\circ$ is

$$A\lambda/2\pi r \cdot \cos 2\pi/\lambda \cdot (ct-r-\delta)$$

where A and δ determine respectively the amplitude and phase.

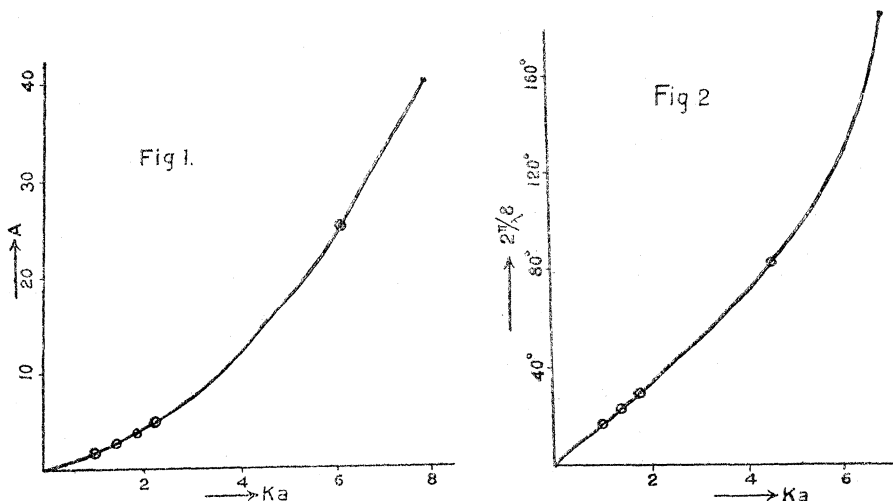


FIG. 1.—Amplitude of scattered wave as a function of ka .

FIG. 2.—Phase of scattered wave as a function of ka .

The particles in the stratum are irregularly arranged, but in the direction of the primary wave-propagation, the secondary waves diverging from the particles are in agreement of phase and can accordingly combine to build up a plane wave-front. The amplitude and phase of this plane wave may be found by integration of the effects of the particles in the stratum in the manner adopted by Rayleigh in his papers on the theory of the light of the sky. The resultant at P of the scattered vibrations which issue from the stratum dx is

$$\begin{aligned} ndx\lambda/2\pi \cdot \int_0^\infty A/r \cdot \cos 2\pi/\lambda \cdot (ct-r-\delta) \cdot 2\pi z dz \\ = ndx\lambda/2\pi \int_x^\infty A/r \cos 2\pi/\lambda \cdot (ct-r-\delta) 2\pi r dr. \end{aligned}$$

In accordance with the usual procedure, the integral is assumed to vanish at the upper limit and reduces to

$$ndx\lambda^2 A/2\pi \cdot \sin 2\pi/\lambda \cdot (ct-x-\delta), \tag{1}$$

On the Transmission Colours of Sulphur Suspensions. 107

A is here the amplitude of the scattered wave due to a particle in the direction of propagation.

The expression for the primary wave is

$$\cos 2\pi/\lambda \cdot (ct-x). \quad (2)$$

Adding (1) and (2) we find that the coefficient of $\cos 2\pi/\lambda \cdot (ct-x)$ is thus altered by the particles in the layer dx from 1 to

$$(1 - An dx \lambda^2 / 2\pi \cdot \sin 2\pi/\lambda \cdot \delta)$$

and the co-efficient of $\sin 2\pi/\lambda \cdot (ct-x)$ from 0 to $An dx \lambda^2 / 2\pi \cdot \cos 2\pi/\lambda \cdot \delta$.

The diminution dE_1 of energy of the primary wave due to the interference with the scattered waves is therefore

$$\frac{dE_1}{E} = -An dx \lambda^2 / \pi \cdot \sin 2\pi/\lambda \cdot \delta.$$

The diminution dE_2 due to reduction in the effective area of the undisturbed wave-front is given by $dE_2/E = -2na^2\pi dx$, where a is the radius of a particle. The total diminution

$$dE/E = (dE_1 + dE_2)/E = -(2n\pi a^2 + An\lambda^2/\pi \cdot \sin 2\pi/\lambda \cdot \delta) dx.$$

The effect of passage of the wave through the successive strata of the turbid medium may be found by integration. We have thus

$$E = E_0 e^{-(2\pi a^2 + An\lambda^2/\pi \cdot \sin 2\pi/\lambda \cdot \delta) nx}, \quad (3)$$

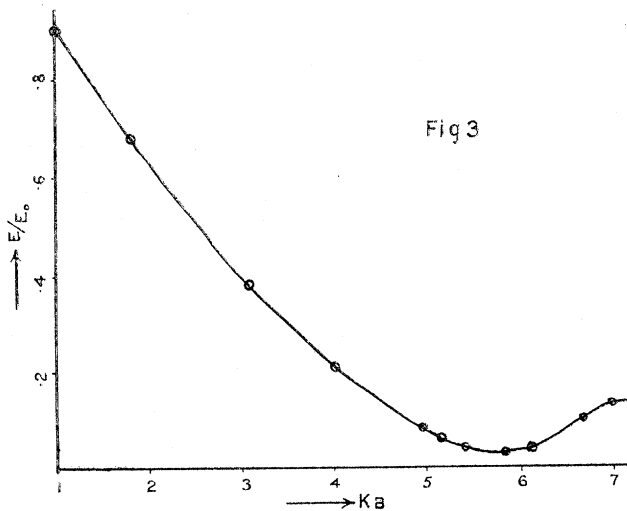
where x is the total thickness. Since the process of integration considers the effect on the transmitted wave arriving at any given stratum of its passage through all preceding strata, the investigation takes into account the influence of multiply-scattered light so far as is relevant to our present purpose, as remarked previously in a footnote. In arriving at the foregoing result, we have tacitly assumed that all the particles are of the same size. In the actual experiment, the size of the particles is variable to some extent, but by taking the effective average size we may obtain a sufficient approximation to the truth; if desired, there would be no difficulty in modifying the formula to obtain a more accurate result by considering separately the effects of particles of different sizes in groups and superposing them to find the resultant.

In applying the formula (3) to the actual conditions of the experiment, it must be remembered that, as the precipitate of sulphur gradually forms, both the average size of the particles and their number per unit volume may vary. A change in the number n would increase or decrease the transmission-coefficient for all wave-lengths simultaneously, whereas the characteristic feature observed in the experiment is the reappearance of the shorter wave-lengths first and of the longer wave-lengths afterwards. The increase in the

108 *On the Transmission Colours of Sulphur Suspensions.*

effective average size of the particles is thus the more important factor in the observed results.

By actually counting, n is found to be of the order 1.5×10^8 per cubic centimetre. Taking the value of A and δ from the graphs in figs. 1 and 2, and the thickness x of the liquid to be 1 cm., the graph in fig. 3 has been



drawn, showing the fraction E/E_0 of the light transmitted as a function of the radius α of the particles. It is seen from the graph that there is an augmentation of transparency when the circumference of the particle is about 6λ . With a greater thickness of the liquid, the failure of transmission and its reappearance at a later stage is even more clearly noticeable. These results are in agreement with observation.

(3) *Concluding Remarks.*

Reference should be made here to the apparent paradox that, though the energy of the waves *scattered* by an individual particle increases continually with its size, nevertheless, the proportion of the energy of the incident light, regularly transmitted by a medium containing a large number of such particles in suspension, may also increase at the same time. This seems at first sight repugnant to the principle of conservation of energy. The paradox is, however, real only if we assume that the energy of the light scattered by n such particles in a unit volume increases *pari passu* with the increase of the energy scattered by an individual particle present in an otherwise homogeneous medium. Such an assumption is not justified, at least in the present case, as it ignores the permanent phase-relationship and

The Photographic Efficiency of Heterogeneous Light. 109

consequent capacity for interference of the scattered and primary waves in the original direction of propagation. The difficulty felt by Rayleigh in explaining the phenomenon studied by Keen and Porter really arose from the tacit assumption made by him that an increase in the energy scattered by an individual particle necessarily connotes an increase in the energy scattered by a medium containing a large number of such particles.

Further, the observed *increase* in the power of transmission of light by the turbid medium at a certain stage necessarily involves on the principle of conservation of energy, a *decrease* in the proportion of energy scattered by it at the same stage. In other words, when a steady parallel beam of light passing through a cell containing the sulphur suspension is focussed on a screen, at the stage at which the transmitted light reappears, there should be a distinct diminution in the intensity of the scattered light also falling upon the screen. The effect to be expected is, however, rather small, and may easily escape observation.

The Photographic Efficiency of Heterogeneous Light.

By F. C. TOY, M.Sc., A.Inst.P.

(Communicated by Prof. A. W. Porter, F.R.S. Received May 12, 1921.)

There are some sources of illumination which are much more active photographically than others, and one of the most active of all artificial sources is the mercury vapour lamp. The energy of the radiation from this lamp is concentrated in a comparatively few spectral lines, and most of these are in that region of the spectrum which is the region of greatest absorption by the silver halide grains of which the photographic emulsion is composed. This, in itself, may be the complete explanation of the intense photographic activity of this particular illuminant, but the question arises as to whether the explanation is, in part, merely the fact that the light is concentrated into a few wave-lengths, apart altogether from any consideration of the absorption coefficient. In other words, a given quantity of radiant energy absorbed in the grains may give a greater photographic effect when it is all of one frequency than when it is a complex radiation such as white light. The object of the present paper is to discuss this question in the light of recent researches on the photographic plate.

This idea has recently been brought forward by Slade and Higson* with

* 'Roy. Soc. Proc.,' A, vol. 98, p. 154 (1920).