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electrodes with occluded gases the less has been the waste of auræ by diffusion &c. During the passage of the current, the auræ and the occluded gases are used up by chemical action, just as the zinc is in an ordinary cell; and as their quantity diminishes, the effective E.M.F. of the voltaic couple formed by the plates also diminishes.

If through leakage of the apparatus, or other causes, atmospheric air obtains access to the liquid surrounding the -electrode, the dissolved oxygen thence resulting will of course tend to reduce the aura of hydrogen by a chemical action of a kind akin to the "local action" of an ordinary voltaic element, *i. e.* not contributing to the work done by the current generated. In this case the rate of fall of the "subsequent polarization" (the electrode not being connected by a wire so as to produce a current) will be more or less enhanced above the rate due to diffusion only, as above described (§ 70); whilst if the electrodes are connected and a current is made to pass, the E.M.F. of the voltaic couple thus produced will diminish more rapidly than would be the case were no dissolved oxygen present in the liquid round the hydrogenplate, just as the zinc of an ordinary cell wastes more rapidly when there is local action than it does when there is not, other things being equal.

XXV. On Copying Diffraction-gratings, and on some Phenomena connnected therewith. By LORD RAYLEIGH, F.R.S., Professor of Experimental Physics in the University of Cambridge.*

IN the Phil. Mag. for February and March 1874 I gave an account of experiments in the photographic reproduction of gratings ruled with lines at a rate of 3000 and 6000 to the inch. Since that time I have had further experience, extending to more closely ruled gratings, and have examined more minutely certain points which I was then obliged to leave unexplained. The present communication is thus to be regarded as supplementary to the former.

Some years ago Prof. Quincke described an unphotographic process by which he had succeeded in copying engraved glass gratings. He began by depositing a thin coating of silver by the chemical method upon the face of the grating. The conducting layer thus obtained was then transferred to an electrolytic cell, and thickened by the deposit of copper, until stout enough to be detached from the glass substratum. In this way he prepared an accurate cast of the

* Communicated by the Author.

glass surface, faced with highly reflecting silver. Since the optical depth of the lines is increased some four times, these gratings usually give much brighter spectra than the glass originals.

Prof. Quincke was kind enough to send me some specimens of his work, giving extremely beautiful spectra. 1 found, however, that, though carefully preserved, these gratings deteriorated after a time, apparently either from insufficient thickness, or from imperfect adhesion of the silver layer. In my own attempts I endeavoured to remedy this defect by not allowing the silver to dry before transference to the electrolytic cell, and by commencing the electric deposit with a *silver* instead of with a copper solution. I did not, however, succeed in finding a thoroughly satisfactory plating-liquid. In the ordinary cyanide solution the silver was at once loosened from the glass. In other solutions the grating could be immersed with impunity, but the film began to strip as soon as the Using *acetate* of silver, however, I was able current passed. to obtain a certain degree of thickening. I also found advantage from commencing the deposit of copper with a neutral solution. After the layer had attained a moderate thickness, its edges were dipped in melted paraffine; and it was then transferred to the usual acid solution of copper. I did not find it necessary to take any precautions against too great an adhesion between the silver and the glass.

These copies are now four years old, and they do not seem A slight yellow tarnish, due probably to have deteriorated. to sulphur, can be removed with cyanide of potassium. There is, however, one defect which I have not been able to avoid. The silver surface is never sufficiently flat to bear much mag-Unless this difficulty can be overcome, the nifying-power. use of such gratings must be limited to cases where brilliancy and not high defining-power is the desirable quality. For most purposes the photographic method of reproduction is to be preferred as far easier and quicker. Among various processes of this kind, I am still inclined to give the preference to that in which collodio-chloride of silver is employed, with subsequent treatment with mercury. The only trouble that I have met with is the tendency of the soluble salts to crystallize in the film; but this can generally be avoided with a little judgment. As these photographs cannot well be varnished, some doubts might have been entertained as to their permanence; but I find that copies now more than seven years old are none the worse. For gratings to be subjected to rough treatment, the various albumen processes offer decided advantages.

In my former paper I stated my opinion that the photographic method of reproduction would be applicable to lines finer than any that I had then tried (6000 to inch). In the summer of 1879 an opportunity afforded itself of submitting the matter to the test of actual trial through the kindness of Mr. Rutherfurd, who presented me with a beautiful glass grating containing nearly 12,000 lines, ruled at the rate of 17,280 to the inch. The copies, taken with suitable precautions to secure a good contact, were completely successful, so far as the spectrum of the first order is concerned. Indeed careful comparison showed no appreciable difference between the defining-power of the original and of the copies; and with respect to brightness some of the copies had the advantage. On a former occasion * I have shown that the theoretical resolving-power in the orange region of the spectrum is equal to that obtainable from a prismatic spectroscope with $12\frac{1}{2}$ per cent. of "extra dense flint;" and I have no reason to This is a think that the actual resolving-power fell far short. considerable result to obtain with a photograph which may be taken in half an hour at a cost of two or three shillings.

The case is different, however, when we turn to the spectrum of the second order. Used in this way the original gives magnificent results; but they are not reproduced in the copies. Some parts of the photograph will sometimes show a faint spectrum of the second order; but it is usually traversed by one or more dark bands, whose nature will presently be examined more at length.

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As a rule, glass (or at any rate transparent) originals only would be used for purposes of reproduction; but as a matter of curiosity I tried what could be done in copying an original ruled on speculum-metal. The specimen experimented upon was similar to my own, both as to the total number of lines and as to the degree of closeness, and belongs to Mr. Spottiswoode, to whom I am indebted for the loan of it. In this case the light of the sun had to pass through the sensitive film before it could reach the speculum-metal; it was then reflected back, and in *returning* through the film impressed the ruled structure. No very brilliant result was to be expected; but I succeeded so far as to obtain a copy which gave very fair results when tested upon the sun.

In my former paper I mentioned that when a spectrum of high order is thrown upon the eye, there usually appear upon the grating a certain number of irregular dark bands. These are the places at which the copy fails to produce the spectrum in question. With lines not closer than 3000 or 6000 * Phil. Mag. Oct. 1879. to the inch, and with reasonably flat glass as support to the photographic film, these bands rarely invade the first or second spectrum. When, however, we come to 17,000 lines to the inch, it requires pretty flat glass and some precautions in printing to keep even the first spectrum free from them.

It was obvious from the first that the formation of these bands was a question of the distance between the ruled surface of the original and the sensitive film; but it is only within the last year or so that I have submitted the point to special experiment. For this purpose I substitute for plane-parallel glass as a substratum for the sensitive film the convex surface of a lens of moderate curvature. As in the experiment of Newton's rings, we obtain in this way an interval gradually increasing from the point of contact outwards, and thus upon one plate secure a record of the effect upon the copy of varying degrees of closeness. When a spectrum of any order is thrown upon the eye, those places upon the grating where the spectrum in question fails appear as dark rings. My first experiment of this kind was made with the Rutherfurd grating, in order principally to find out how close a contact was really necessary for copying. From the diameter of the first dark ring, in conjunction with a rough estimate of the curvature of the lens, I concluded that the interval between the surfaces should nowhere much exceed $\frac{1}{10000}$ of an inch. It appeared at the same time that the chance was remote of obtaining a satisfactory performance in the spectrum of the second order. About this time the theoretical views occurred to me which will presently be explained, and I purposed to check them by more careful measurements than I had yet attempted. In the course of last summer, however, I found accidentally that Fox Talbot had made, many years ago*, some kindred ob-servations; and the perusal of his account of them induced me to alter somewhat my proposed line of attack. It will be convenient to quote here Fox Talbot's brief statement :----

"About ten or twenty feet from the radiant point, I placed in the path of the ray an equidistant grating † made by Fraunhofer, with its lines vertical. I then viewed the light which had passed through this grating with a lens of considerable magnifying-power. The appearance was very curious, being a regular alternation of numerous lines of bands of red and green colour, having their directions parallel to the lines of the grating. On removing the lens a little further from the grating, the bands gradually changed their colours,

* Phil. Mag. Dec. 1836.

† A plate of glass covered with gold leaf, on which several hundred parallel lines are cut, in order to transmit the light at equal intervals.

and became alternately blue and yellow. When the lens was a little more removed, the bands again became red and green. And this change continued to take place for an indefinite number of times, as the distance between the lens and grating increased. In all cases the bands exhibited two complementary colours.

"It was very curious to observe that, though the grating was greatly out of the focus of the lens, yet the appearance of the bands was perfectly distinct and well defined.

"This, however, only happens when the radiant point has a very small apparent diameter, in which case the distance of the lens may be increased, even up to one or two feet from the grating, without much impairing the beauty and distinctness of the coloured bands. So that if the source of light were a mere mathematical point, it appears possible that this distance might be increased without limit; or that the disturbance in the luminiferous undulations caused by the interposition of the grating continues indefinitely, and has no tendency to subside of itself."

It is scarcely necessary to point out that what was seen by the eye in this experiment in any position of the magnifying lens was the same as would have been depicted upon a photographic plate situated at its focus, at least if the same kind of rays had been operative in both cases. Talbot's observations are therefore to the point as determining the effect of varying intervals in photographic copying.

On the whole the above description agrees well with what I had expected from theory. It is indeed impossible to admit that the red and green coloration could disappear and revive an *indefinite* number of times. The appearance of colour at all shows that the phenomenon varies with the wave-length, and accordingly that it would (as in all such cases when white light is used) ultimately be lost. Besides the limit imposed by the apparent magnitude of the source of light, there must be another depending upon the variation of wave-length within the range concerned.

In trying to repeat Talbot's experiment I found that even the 3000-to-the-inch grating was too fine to be conveniently employed; and eventually I fell back upon a very coarse grating made some years ago by photographing (with the camera and lens) a piece of striped stuff. By comparison of coincidences with the divisions of fine ivory scale (vernier fashion), the period was determined as 0104 inch. As a source of light I used a slit placed parallel to the lines of the grating, and backed by a fish-tail gas-flame seen edgeways. In order to observe the appearances behind the grating, a lens of moderate magnifying-power was sufficient. This lens was moved gradually back until something distinctive was seen; and the distance between the lens and the grating was then measured and recorded. In order to render the light more nearly monochromatic, pieces of red or green glass were usually held in front of the eye.

With red light the nearly equal bright and dark bars are seen in focus when the distance of the lens from the grating is $1\frac{3}{4}$ inch. As the distance is increased, the definition deteriorates, and is worst at a distance of $3\frac{5}{8}$. In this position the proper period (0104 inch) is lost, but subordinate fluctuations of brightness in shorter periods prevent the formation of a thoroughly flat field of view. As the distance is further increased, the definition appears to improve, until at distances $5\frac{3}{4}$ and $6\frac{3}{4}$ it is nearly as good as at first. The definition in an intermediate position such as $6\frac{1}{4}$ is distinctly inferior, but is far from being lost as in position $3\frac{5}{8}$. From the theoretical point of view, to be presently explained, these two positions of extra good definition are not to be distinguished. They relate rather to the sharpness of the edge of the band, than to any special prominence of the proper period. At a distance of $7\frac{1}{2}$ we have again a place of worst definition, at $10\frac{1}{4}$ a revival, and so on. These alternations could be traced to a distance of *nine* feet behind the grating.

The accompanying table gives the positions of best and worst definitions for red and green light respectively. Of these the places of *worst* definition could be observed with the greater accuracy; but none of the observations have any pretensions to precision. The star indicates the position for focus.

Red light.		Green light.	
Best.	Worst.	Best.	Worst.
*13	3 §	*11	$-3\frac{3}{4}$
$5\frac{3}{4}, 6\frac{3}{4}$	71/2	$6\frac{1}{4}$	85
10‡	12 1	11	14 <u>1</u>
$15\frac{1}{8}$	17	$16\frac{1}{2}$	$19\frac{3}{4}$
$19\frac{3}{4}$	$21\frac{7}{8}$	$22\frac{1}{8}$	$25\frac{1}{4}$
$24\frac{3}{4}$	27	$27\frac{3}{4}$	$31\frac{1}{2}$
$29\frac{1}{4}$	$32\frac{1}{8}$	$33\frac{1}{4}$	37
34 1	$37\frac{1}{2}$		

It is evident that the positions for red light gradually fall quite away from the corresponding positions for green light.

At $19\frac{3}{4}$, for example, if we use a green glass, we lose sight of the proper period, and have before us an almost uniform field; but if without making any other change we substitute a red glass for the green one, we see the bands again with great At about the greatest distance included in the distinctness. table the positions of best definition are again in coincidence; but here there is an important remark to be made. If, using the green glass, we adjust a needle-point to the centre of a bright band, we find, on substituting the red glass, that the needle-point is now in the centre, not of a bright, but of a dark The fact is that at every revival of definition the image band. changes sign, in the photographic sense, from positive to negative, or from negative to positive-a clear proof that the appearance in question is not a mere *shadow* in any ordinary sense of the term.

With respect to the numerical values of the distances given in the table, theory indicates that the interval from worst to worst or from best to best definition should be a third proportional to the period of the grating d, and the wave-length of the light λ , *i. e.* should be equal to d^2/λ . In the case of red light, the mean interval from worst to worst is 4.8 inches, and from best to best 4.7. The corresponding numbers for green light are 5.5 and 5.3. In the subsequent calculation, I have used the first stated intervals as probably the more correct.

For the grating employed the actual value of d was $\cdot 0104$ inch; but a small correction is required for the want of parallelism of the light. The distance of the source was about 27 feet; so that, as the mean distance behind the grating at which the appearances were observed was $1\frac{1}{2}$ foot, the above value of d must be increased in the ratio of $28\frac{1}{2}$ to 27. Thus for the effective d in centimetres, we get

$$2.54 \times \frac{57}{54} \times .0104.$$

Calculating from this and from the observed intervals a by means of the formula $\lambda = d^2/a$, we get in centimetres

$$\lambda_{(\text{red})} = 6.40 \times 10^{-5}, \ \lambda_{(\text{green})} = 5.59 \times 10^{-5}.$$

Direct determination of the mean wave-lengths of the lights transmitted by the red and green glasses respectively gave

$$\lambda_{(red)} = 6.64 \times 10^{-5}, \ \lambda_{(green)} = 5.76 \times 10^{-5}$$

The true wave-lengths are certainly somewhat greater than those calculated from Talbot's phenomenon; but the difference is perhaps hardly outside the limits of experimental error. If the measurements were ever repeated, it would be advisable to use a collimating lens as well as a more accurate grating.

The problem of determining the illumination at various points behind a grating exposed to a parallel beam of homogeneous light, could probably be attacked with success by the usual methods of physical optics, if it were assumed that the grating presented uniform intervals alternately transparent and opaque. Actual gratings, however, do not answer to this description, and, indeed, vary greatly in character. I have therefore preferred to follow the comparatively simple method, explained in my book on Sound, §§ 268, 301, which is adequate to the determination of the leading features of the phenomenon.

Taking the axis of z normal to the grating, and parallel to the original direction of the light, and the axis of x perpendicular to the lines of the grating, we require a general expression for the vibration of given frequency which is periodic with respect to x in the distance d. Denoting the velocity of propagation of ordinary plane waves by a, and writing $\kappa = 2\pi/\lambda$, we may take as this expression

$$\begin{aligned} A_0 \cos(\kappa at - \kappa z) + A_1 \cos\left(\frac{2\pi x}{d} + e_1\right) \cos\left(\kappa at - \mu_1 z\right) \\ + B_1 \cos\left(\frac{2\pi x}{d} + e_1'\right) \sin(\kappa at - \mu_1 z) \\ + A_2 \cos\left(\frac{4\pi x}{d} + e_2\right) \cos(\kappa at - \mu_2 z) \\ + B_2 \cos\left(\frac{4\pi x}{d} + e_2'\right) \sin(\kappa at - \mu_2 z) + \dots, \end{aligned}$$

where

$$\mu_1^2 = \kappa^2 - \frac{4\pi^2}{d^2}, \quad \mu_2^2 = \kappa^2 - \frac{4 \cdot 4\pi^2}{d^2}, \quad \mu_3^2 = \kappa^2 - \frac{9 \cdot 4\pi^2}{d^2}, \text{ &c.}$$

The series is to be continued as long as μ^2 is positive, *i. e.* as long as the period of the component fluctuations parallel to *x* is greater than λ . Features in the wave-form whose period is less than λ cannot be propagated in this way, but are rapidly extinguished.

The intensity of vibration, measured by the square of the amplitude, is

$$\begin{bmatrix} A_0 + A_1 \cos\left(\frac{2\pi x}{d} + e_1\right) \cos(\kappa z - \mu_1 z) \\ + B_1 \cos\left(\frac{2\pi x}{d} + e_1'\right) \sin(\kappa z - \mu_1 z) \end{bmatrix}$$

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$$+ A_{2} \cos\left(\frac{4\pi x}{d} + e_{2}\right) \cos(\kappa z - \mu_{2}z) + \dots]^{2}$$

$$+ \left[-A_{1} \cos\left(\frac{2\pi x}{d} + e_{1}\right) \sin(\kappa z - \mu_{1}z)$$

$$+ B_{1} \cos\left(\frac{2\pi x}{d} + e'\right) \cos(\kappa z - \mu_{1}z)$$

$$- A_{2} \cos\left(\frac{2\pi x}{d} + e_{2}\right) \sin(\kappa z - \mu_{2}z) + \dots]^{2}.$$

In order to apply this result to our present question, it is supposed as a rough approximation that the terms with suffixes higher than one may be omitted. We thus obtain

$$\begin{aligned} A_0^2 + \frac{1}{2}A_1^2 + \frac{1}{2}B_1^2 + 2A_0A_1\cos\left(\frac{2\pi x}{d} + e_1\right)\cos(\kappa z - \mu_1 z) \\ + 2A_0B_1\cos\left(\frac{2\pi x}{d} + e_1'\right)\sin(\kappa z - \mu_1 z) \\ + \frac{1}{2}A_1^2\cos\left(\frac{4\pi x}{d} + 2e_1\right) + \frac{1}{2}B_1^2\cos\left(\frac{4\pi x}{d} + 2e_1'\right), \end{aligned}$$

which as a function of z is periodic with a period determined by $\kappa z - \mu_1 z = 2\pi$, or λ

$$=\frac{\lambda}{1-\sqrt{\left(1-\frac{\lambda^2}{d^2}\right)}}$$

In the cases with which we are concerned λ^2 is small in comparison with d^2 , so that approximately $z = 2d^2/\lambda$. So far, then, as this theory extends, the phenomena behind the grating are reproduced with every retreat through a distance $2d^2/\lambda$; but, on account of the terms omitted, this conclusion does not apply to the subordinate periods (on which depends the performance of a copy in the spectra of higher order); nor does it apply rigorously even to the principal period itself.

Similar results to those given by direct inspection on the coarse grating have been obtained by photographic copying of finer ones, a lens (as already explained) being substituted for flat glass as a support for the sensitive film. When the copy is held so that the spectrum of the first order is formed upon the eye, several dark rings are visible, separated by intervals of brightness. With the 6000 Nobert the diameter of the first dark ring was '54 inch, and at the centre round the point of contact there was a dark spot nearly as dark as the ring. In the second and third spectra the centres were also dusky, though not so black as in the first. The diameter of the first dark ring in the second spectrum was '30 inch.

The occurrence of a dark centre is a point of interest, as showing that for purposes of reproduction it is possible for the contact to be too close, though I do not remember to have met with this in practice; and theoretically it is what would be expected when we consider that the original does not act According to this view a different result should by opacity. be obtained in copying an opaque grating; and such I have For this purpose I employed a copy of found to be the case. the same 6000 Nobert, taken some years ago on a tannin plate, and prepared the photographic film on the same lens as before. When the resulting photograph was examined, the spectra of the first three orders showed bright centres. The diameter of the first dark ring in the first spectrum was $\cdot 44$ inch-smaller than before.

With the 3000 Nobert in place of the 6000 the ring-system is formed on a larger scale. The centres for the first four spectra are black, with the exception of the actual place of contact, where evidently the collodion film was impressed mechanically. The diameter of the first dark ring in the first spectrum is $\cdot 90$ inch, not quite the double of $\cdot 54$ inch, although the same lens as before was used. In the second spectrum the diameter of the first dark ring is $\cdot 56$ inch, and in the third spectrum $\cdot 40$ inch.

Interesting as these bands may be in theory, they are to be avoided as much as possible in the practical reproduction of gratings, not merely because a part of the area is lost, but also on account of the reversal which takes place at every revival of brightness. Without having examined the matter very closely, I had generally found the performance of gratings which showed these bands to be inferior; and now it would seem that the explanation is to be found in the above-mentioned reversals, which could not fail to interfere with the resolving-power.

During my early experiments it happened once that in the course of printing an accidental shifting took place, leading to the impression of a double image. A more perfect result was afterwards obtained by intentionally communicating to the plates a slight relative twist in the middle of the exposure. When a spectrum from such a grating is thrown upon the eye, parallel bars are seen perpendicular to the direction of the grooves; but the number and position of these bars depend upon the order of the spectrum. In one case twentyfive bars were counted in the first spectrum, and twice that number in the second. But it is unnecessary to dwell further upon these observations, as they correspond exactly to what the ordinary theory of gratings would lead us to expect.

January 29.

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