going two series accords completely with their analytical separation into two groups, the cerium earths lighter and the ' yttrium ' earths heavier than gadolinium. Details of the division of the rare earths into the two series on other chemical and crystallo‑graphic grounds will shortly be submitted to the Chemical Society.　　　　　　J. D. MAIN SMITH.

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Sept. 20.

## The Films Responsible for Oxidation Tints on Metals.

THE colours produced by heating metals in air have long attracted interest. Within the last three years it has proved possible in two cases (lead and iron) to separate from the basis metal the oxide-films responsible for these tints. In the case of lead, which is liquid at the requisite temperatures, the oxide-film is lifted off the molten metal on glass (*Proc. Roy. Soc.*, A, **107**, 228; 1925), whilst in the case of iron the method employed is that originally worked out for the isolation of the much thinner, invisible skin responsible for the passivity of iron treated with oxidising agents. This method (*Jour. Chem. Soc.*, 1020; 1927) consists in undermining the oxide-film by dissolving away the metal below it with iodine solution, so that the film comes peeling off in curling fragments, which can be washed by decantation and examined under the microscope.

The chemical aspects of the matter have been discussed in the two papers quoted above, but there are certain physical observations which may perhaps deserve to be put on record. There is a remarkable difference between the oxide-films stripped from lead and iron respectively. The lead oxide film is highly transparent, and the film itself, when separated from the metal, shows interference colours, depending on the thickness, the tint by reflected light being always complementary to the tint by transmitted light. As a result of the transparency, the higher order colours corresponding to thick films can easily be observed, the second-order tints being as vivid as the first-order colours; at greater thicknesses third and fourth orders appear. The sequence of tints is essentially the same as that exhibited by silver exposed to iodine vapour, silver iodide also being a transparent substance.

When we come to iron, however, the state of affairs is different. Viewed by reflected light, the film fragments show a brilliant metallic lustre, and in some cases might easily be mistaken for metallic iron; they retain all the surface irregularities displayed by the original metallic surface before its conversion into oxide; thus if the abrasive treatment originally used to produce a clean metallic surface has left a series of microscopic grooves and ridges on the metal, the films are crenulated in a manner which faithfully reproduces these grooves and ridges. However, on altering the illumination so that the films are viewed by transmitted light, it is at once seen that they consist of a transparent substance, with only occasional opaque points consisting mainly of minute spots of residual metallic iron embedded in the oxide and usually arranged in lines following the grooving (these particles of residual iron are best shown up as expanding blue spots by treating the film fragments with an acid solution of potassium ferricyanide). But the transparency of the oxide films is distinctly less perfect than that of the corresponding lead oxide films; even the film responsible for the first-order yellow tint has a perceptible yellowish-grey colour, clearly due to specific absorption, whilst the films become darker and darker as we proceed along the sequence, so that the films to which the second-order

tints are attributable show a quite dark brownish-grey appearance by transmitted light.

This specific absorption is more than sufficient to mask any colour due to interference, and consequently the films—unlike those separated from heated lead—do not themselves show bright tints, although the ' character ' of the brown colour varies slightly with the thickness—possibly as the result of interference of the ' thin-film type.' It may perhaps seem curious that the films should nevertheless produce colours when in contact with the metal. In my opinion an explanation can be given. Any theory based on interference between the light reflected respectively from the outer and inner surfaces of the film would lead us to expect that a *slight* degree of opacity will, at low film thicknesses, actually favour the production of colour, since it will tend to reduce the inequality between the intensity of the two reflections ; when, however, the film is off the metal, the two reflections would be approximately equal in intensity in the case of a highly transparent film, and the slightest opacity will be unfavourable to the effect. The serious opacity of the thicker films of iron oxide explains why the second and third order tints—so conspicuous in the case of lead—are badly developed on iron, even when the film is still on the metal. After the end of the first - order tints, the colours become faint and are modified somewhat by the specific colour of the scale, which, although slightly yellowish by transmitted light, is a rather bluish grey by reflected light. Nevertheless, there has been no difficulty in tracing the sequence as far as the third-order red, the sequence being essentially the same as that shown by lead or copper.

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## Adsorption of Gases on the Surface of Mercury.

CERTAIN methods of measuring the surface tension of mercury, especially the ' big-drop ' method as used by Popesco (*Ann. de Physique*, **3**, p. 402 ; 1925), appear to show that the presence of air or other gas increases the surface tension of a freshly formed surface by about 100 dynes. The ' drop-weight ' method, on the other hand, shows a difference of only a few dynes between the values in air and *in vacuo*, and this indeed in the opposite sense to that indicated above (Harkins, *Jour. Am. Chem. Soc.*, Dec. 1920). Observations by the writers using the same mercury in order to measure its surface tension by the above as well as other methods show that the differences in the measured values of the surface tension are due to differences in the method and not to differences in the quality of mercury (*Trans. Faraday Soc.*, May 1927).

It is therefore especially important to gain some information as to the adsorption of gas by a freshly formed mercury surface. This has now been accomplished by applying to gases a method similar to that used by Schofield for solutions (*Phil. Mag.*, Mar. 1926). A shower of about 500 drops per second of mercury falls down a vertical tube about 50 cm. long to the middle of which is sealed a side-tube. Through this side-tube is fed a slow stream of either hydrogen or argon containing a small percentage of carbon dioxide. The stream of gas divides and is taken from the vertical tube by two outlets, one near the top and the other near the mercury surface at the bottom of the tube. From these outlets the gas passes to the tubes of a Rayleigh interferometer.

Any gas adsorbed by the falling drops is given up at the bottom of the tube, and if the carbon dioxide