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The Effect of Impurities on the Whiteness of Lanthanum Oxide

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The present paper will investigate how the whiteness of lanthanum oxide is affected by the presence of minor amounts of three common impurities, praseodymium, neodymium and calcium; the influence is expressed in terms of the Munsell Value scale.

Lanthanum oxide, La_2O_3, is a white, amorphous powder which has increasingly been used in many fields of industries; for instance, using it the glass industry has produced a silica-free optical glass with a high refractive index. The purity of the commercially available material is usually 99.5% or more.

However, it has been accepted that, from an industrial point of view, one of the most important factors in evaluating a white powdery product on the market is its appearance of whiteness. The case of lanthanum oxide is no exception; a visual comparison is one of the usual practices in judging the quality or marketability of the white product.

The element has been separated from a rare earth mixture, itself derived from monazite sand and consisting of the rare earth elements from La through Lu, by basicity separations[1,2] or by fractional crystallization.[3] Praseodymium and neodymium are frequent contaminants in the lanthanum due to the fact that these two elements are the closest neighbors of the lanthanum in the La-Lu series and so are the most difficult to separate.

1) E. V. Klever and B. Love, "The Technology of Scandium, Yttrium and the Rare Earth Metals," Pergamon Press, London and New York (1963), p. 19.

2) C. A. Hampel, *Glass Ind.*, **41**, No. 1, 15 (1960).

3) F. H. Spedding and A. H. Daane, "The Rare Earths," John Wiley and Sons, New York and London (1961), p. 137.

While the oxides of La, Ce^{3+}, Tb, and Lu are colorless, the coloring is most distinct in the case of Pr_6O_{11} and Nd_2O_3; Pr_6O_{11} is black, and Nd_2O_3 is lavender blue.[4] Therefore, the presence of these two elements in the La_2O_3, even in small quantities, will appreciably degrade the whiteness of the product; such presence usually gives a grayish shade to the product, which would otherwise be pure white.

Still another impurity which commonly accompanies this element is calcium coming from the monazite sand and the processing water used in the manufacturing plant. Calcium is also close to lanthanum in many characteristics, such as its basicity, its separability with ion exchange resins, and the solubility product of oxalate. Although the removal of calcium from the lanthanum is of prime importance for the manufacturer, the influence of this element on the coloring of La_2O_3 has previously been frequently overlooked, for the calcium oxide is also white in itself.

This paper will present the results of a study whereby a color difference meter was used to characterize the interdependence of the influence of three common impurities, Pr, Nd, and Ca, on the coloring of highly pure lanthanum oxide in an attempt to provide a convenient criterion in terms of the value scale in the Munsell color system. The purpose here is to establish a practical measure for judging which one of these three elements is the major source of the coloring and to help to improve the quality of the La_2O_3 product in terms of its whiteness as well as of its chemical purity.

Experimental

Materials. Spectrographic-grade highly pure oxides of lanthanum, neodymium, and praseodymium were commercially available from the Lindsay Chemical Division, American Potash and Chemical Corp., and from Johnson, Matthey & Co. Lanthanum oxide was graded as 99.997% La_2O_3, while praseodymium oxide and neodymium oxide were 99.9% Pr_6O_{11} and 99.9% Nd_2O_3 respectively. As for the calcium component, reagent-grade calcium oxide was used. Spectrographic examinations showed no evidence of unnecessary elements in this material.

Procedures. The component oxides are weighed into a beaker, dissolved with dilute hydrochloric acid, and stirred. An oxalic acid solution was then added, and a mixed oxalate precipitate was obtained and ignited at about 1000°C to give several samples of lanthanum oxides contaminated, to several degrees, with small amounts of neodymium, praseodymium, and calcium oxides. Contaminations with Pr_6O_{11} to the extent of 0.15%, Nd_2O_3 0.35%, and CaO 1.0% of the lanthanum oxide produced a dark-colored sample which no longer bore a commercial value in its appearance. The degradation of the lanthanum oxide due to the artificially incorporated impurities was measured with a Color Difference Meter using the Munsell value scale, and the values *versus* the impurity contents were plotted. However, no appreciable differences in the Chroma and Hue scales were observed because the produced colors were solely gray or dark, well fitting into the value scale from about 6.5 to 9.5, the latter of which was the reading for the lanthanum oxide as received.

4) *E.g.*, Catalogue for Products of The Rare Earth Group, Johnson, Matthey & Co., London.

Results and Discussion

Figure 1 shows the value of the lanthanum oxide against the CaO content in the presence of Nd_2O_3 and/or Pr_6O_{11}. It may be observed from curve (1) that the presence of 0.5% Nd_2O_3 exhibits no appreciable effect on the appearance of La_2O_3, even with an increase in the CaO content up to 1.0%. Therefore, a rather low-purity lanthanum oixde (about 98.5% La_2O_3) can retain its white appearance, with a value of about 9.0, if the La_2O_3 contains no impurities other than Nd_2O_3 and CaO.

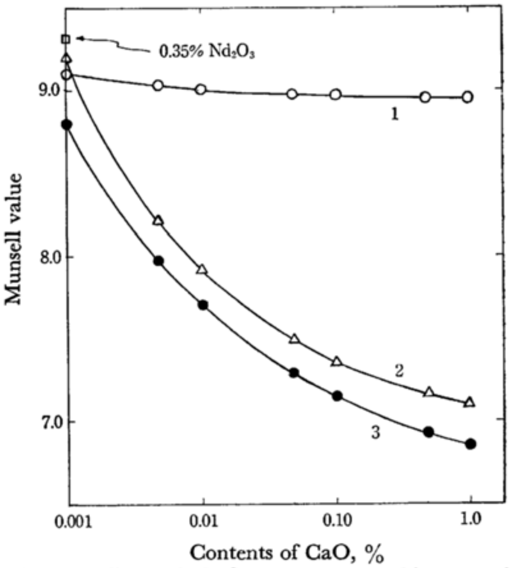

Fig. 1. Effect of CaO content on whiteness of La_2O_3 contaminated with Pr_6O_{11} and/or Nd_2O_3 expressed in terms of the Munsell Value scale. (1): La_2O_3-0.5% Nd_2O_3 system, (2): La_2O_3-0.15% Pr_6O_{11} system, and (3): La_2O_3-0.15% Pr_6O_{11}-0.35% Nd_2O_3 system.

On the other hand, the situation is quite different in the case of Pr_6O_{11} as may be observed from curve (2). A contamination of La_2O_3 with only 0.15% Pr_6O_{11} and 0.01% CaO has much degraded the white appearance down to the value of 7.9, although the net La_2O_3 content is still higher (being 99.8% La_2O_3). It may also be seen from curve (2) that the presence of CaO to the extent of 1.0% together with the Pr_6O_{11}, gives the low value of 7.1, with which the product may no longer be marketable. It is to be noted from curves (1) and

(2), however, that the presence of 0.15% Pr_6O_{11} is less detrimental than that of 0.5% Nd_2O_3 if the CaO is not present at all or if only a trace is present.

From the initial position of curve (3) on the ordinate of Fig. 1 it may be seen that the combination of 0.15% Pr_6O_{11} and 0.35% Nd_2O_3 is more detrimental than 0.5% Nd_2O_3 alone. It can be naturally expected that the individual effect of 0.35% Nd_2O_3 will be less harmful than that of 0.5% Nd_2O_3, which gives a value reading of 9.3. 0.15% Pr_6O_{11} without calcium also does practically no harm, giving 9.2 However, the starting point of curve (3), positioned on the ordinate at a value less by about 0.3 than curves (1) and (2), indicates that the interaction of 0.35% Nd_2O_3 and 0.15% Pr_6O_{11} exists in spite of the fact that these elements individually behave much less harmfully. The additions of CaO to the La_2O_3-Pr_6O_{11}-Nd_2O_3 system remarkably decrease the value of the whiteness, and the curve (3) parallels the curve (2) down to about 6.9 with 1% CaO.

Most commercial rare-earth salts contain individual elements in about the same ratio as the ore treated.[5] After cerium has been removed by oxidation and hydrolysis, therefore, praseodymium and neodymium are the major impurities of lanthanum remaining until the last stages of the purification process, because these two elements are close to lanthanum in chemical and physical characteristics except in color. Moreover, they are present in the raw materials in amounts next to that of lanthanum. On the other hand, the rest of the impurities, from Sm through Sc, are relatively easier to separate because of their considerable difference in characteristics and their small amounts. Although it has been conventionally thought that the best way to obtain a pure white lanthanum oxide is simply to make the net La_2O_3 content as free as possible from these rare earth impurities, the results of Fig. 1 show that there is a possibility of a sample with 99.8% La_2O_3 (0.15% Pr_6O_{11}+ 0.01% CaO) being worse in color than one with 98.5% La_2O_3 (0.5% Nd_2O_3 + 1.0% CaO). It follows, accordingly, that emphasis should be placed on the removal of calcium in many cases in order to obtain a La_2O_3 product of high quality in both whiteness and chemical purity.

5) J. G Parker, "Mineral Facts and Problems, Rare Earths," Bull. 630, Bureau of Mines, 1965 ed., p. 753.

Summary

The detrimental effects of three common impurities, praseodymium, neodymium, and calcium, on the coloring of lanthanum oxide were investigated in terms of the Munsell value scale, using a color difference meter. The co-existence of praseodymium and calcium was most distinct in degrading the white color of lanthanum oxide, while neodymium was a minor coloring source even when combined with calcium. The effect of praseodymium present in a minor amount was not very pronounced without the simultaneous presence of calcium. The combination of praseodymium and neodymium did the most harm in the presence of calcium.