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THE INVESTIGATION OF COLOR MODIFICATION AS A RESULT OF SOLID SOLUTION

BY

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A

THESIS

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Approved by Paul G. Herold

Professor of Ceramic Engineering

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PURPOSE OF THE INVESTIGATION:

To the ceramic industry, color has long been one of its chief problems, not only in reproducing colors in the many complex silicate structures but in the development of stains that are stable at high temperatures and that are economically feasible for mass production. At the present time a stable high temperature red or yellow would be very desirable.

Solid solution has been employed in ceramics to modify and thereby provide ceramic materials of different physical characteristics. The limited data available with respect to such solid solution serves to indicate that perhaps this state may serve as an important means of modifying the characteristic color of the transition element oxides. Any modifications that can be shown to exist will be important academically, if not commercially.

REVIEW OF LITERATURE:

There is little in the literature that gives much light upon the development of colors as a result of solid solution. Certain of the two component systems have been studied in the trend of the phase rule from pure scientific points of view, that is, with reference to the nature of the melt and the crystalline portions present at various temperatures and percent compositions.

Hedvall has studied the systems of CoO-MgO,(1) and MgO-NiO,(2) and Passerini has made similar studies;(3) however, in both cases these investigators were interested only in the crystal structure and the determination of the lattice constants. No mention has been made of the color of the resulting solid solution or any practical application of the systems.

A further literature review of color characteristics and measurements, as well as certain criteria for solid solution will be included in the introduction.

INTRODUCTION:

The term "color" is used in three different senses.(4) To the chemist, a color is simply a material such as a dyestaff. To the physicists, "color" is practically synonymous with light, and both are described in objective terms by the spectral distribution of energy of the radiation in question. To the psychologist, the term "color" denotes the subjective sensation produced in the brain of a human observer and is considered a result of a physical stimulus. All of these meanings for color make sense to those who

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(1) Hedvall, Zeitsch. Anorg. Chem., 1914, p. 296

(2) Hedvall, Zeitsch. Anorg. Chem., 1918, Vol. 103, p. 249

(3) Passerini, Gazz. Chem. Italia, Vol. 59, 1929, p. 144

(4) Hardy and Perrine, Principles of Optics, p. 296, McGraw Hill Book Company

use them and there is a good deal of sense to all of them. Naturally, in the specification and evaluation of the appearance of certain materials it would be desirable to be able to take some one meaning for the term "color" but all three definitions of color are so firmly embedded in our language that there is little hope of achieving a uniform usage for the term "color", however desirable it might be from the standpoint of avoiding confusion. In view of this fact Dr. Deane B. Judd of the National Bureau of Standards has suggested psychological and scientific definitions of color.(5) As a psychological definition Judd proposes that "color is that aspect of the appearance of objects and lights which depend upon the spectral composition of the radiant energy reaching the retina of the eye and upon its temporal and spatial distribution thereon". As a scientific definition he proposes that "color is that aspect of the appearance of light which depends upon its spectral composition". Color by this latter definition may be evaluated by physical measurements in relation to some reference material, and it is with this type of color measurements that this investigation is concerned.

The visual stimulation that results when a material is looked upon is dependent upon the source of illumination.(6)

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(5) A.S.T.M. Symposium on Color, Deane B. Judd, p. 1, 1941

(6) A. C. Hardy, Handbook of Colorimetry, Tech. Press, Cambridge, Mass.

Hence, if a surface is illuminated by light of substantially a single wave length, it will reflect only light of this wave length.

Since daylight consists of a mixture of all the components of the spectrum in nearly equal proportions an extensive investigation as to the distribution of energy in the spectrum of daylight has been carried on over long periods of time. These investigations consisted of dispersing the light into a spectrum by means of a prism and then isolating each spectral region and determining the amount of energy present in each region from the reading of a sensitive temperature measuring device. As a result of this work a filter has been prepared which when used with a tungsten lamp operated at the right temperature provides a source that is a close approximation to average daylight. This source has been adopted as an international standard of illumination to be used for the purposes of colorimetry except when special cases require other sources. The standard is known as I.C.I. Illuminant C. Two other standards have also been adopted and are designated as Illuminant A and Illuminant B. The former represents a source having an energy distribution similar to that of a gas filled tungsten lamp; the latter is an approximate representation of a mean noon sunlight.

From the standpoint of actual physical measurements the most important problem is the interpretation of spectrophotometric data.(7) The young-Helmoltz theory provides a satisfactory solution. Founded on experimental data, this theory says that any color stimulus can be matched visually by a mixture of the proper amounts of three arbitrarily chosen stimuli, which are called primaries. The unknown color can then be specified by three letters, x, y, and z. These are known as the tristimulus values, and each represents the amount of one of the primary stimuli. The tristimulus values that were adopted by the International Commission on Illumination in 1931 for the various spectrum colors are indicated graphically in figure 1. Here the values $\bar{x}$, $\bar{y}$, and $\bar{z}$ indicate the amount of each of the I.C.I. primaries that is required to color match a unit quantity of radiant energy of the various wave lengths.

Another method of color expression is that of trichromatic coefficients which are derived from the tristimulus values and are calculated as follows:

$$x = \frac{\bar{x}}{\bar{x} + \bar{y} + \bar{z}}, \quad y = \frac{\bar{y}}{\bar{x} + \bar{y} + \bar{z}}, \quad z = \frac{\bar{z}}{\bar{x} + \bar{y} + \bar{z}}$$

where x, y, z are the trichromatic coefficients, $\bar{x}$, $\bar{y}$, $\bar{z}$ are the tristimulus values.

It can be seen that x, y, and z are the percentages of each of the primaries that must be added in order to color match a particular quantity of radiant energy. Thus, $x + y + z = 1$ and to express a particular color only

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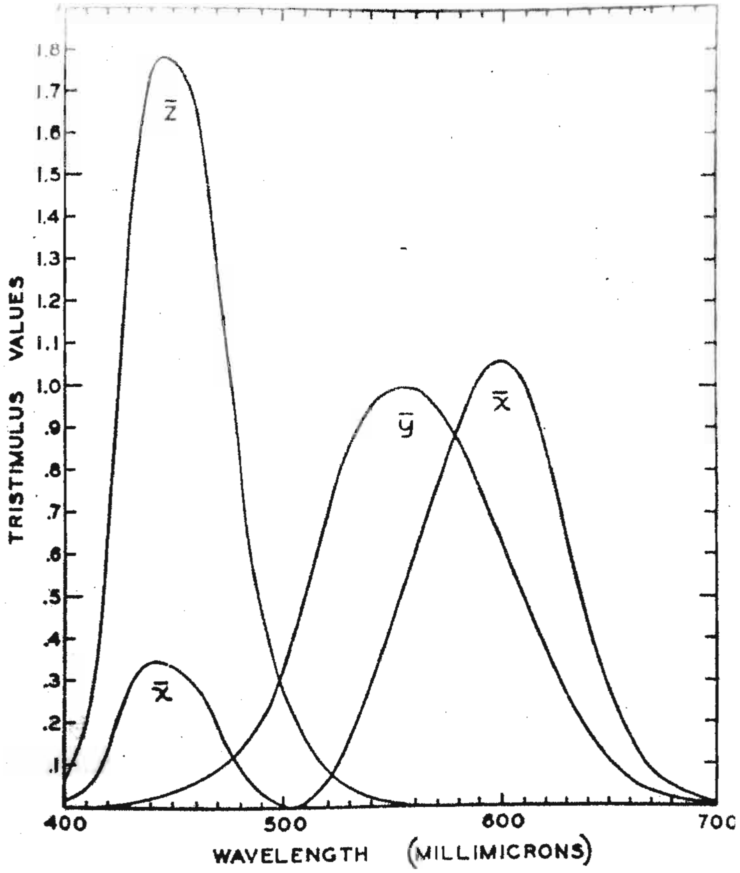
(7) Hardy and Perrine, Principles of Optics, p. 298, McGraw Hill



[redacted]

Tristimulus values for the various spectrum colors. The values of $\bar{x}$, $\bar{y}$,

FIGURE 1

two of the three values need be given.

When a color difference exists between two colors the tristimulus values do not readily show this difference, whereas the trichromatic coefficients immediately bring this fact forward. The tristimulus values, however, do indicate directly the value of the relative brightness.

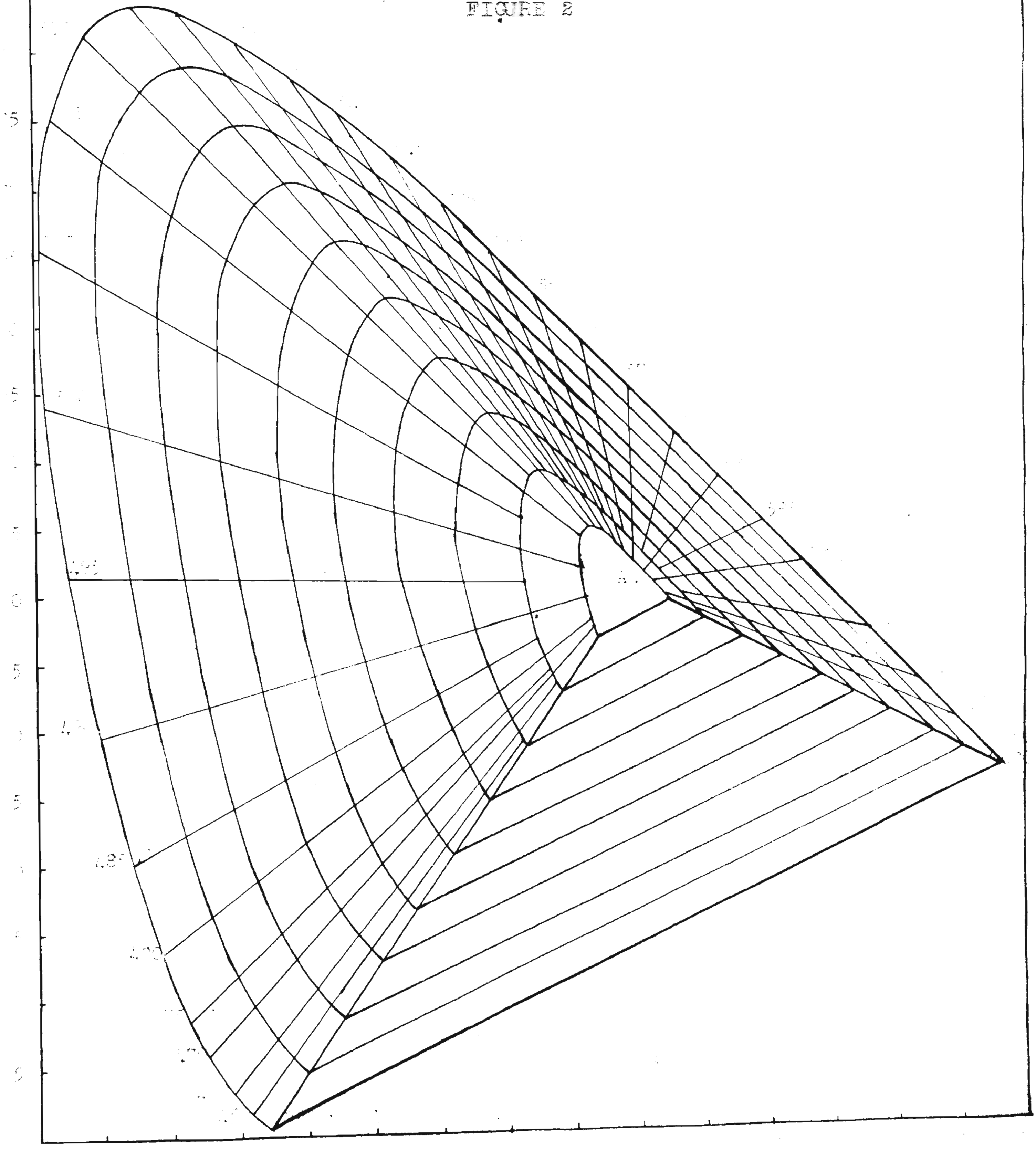
The I.C.I. primaries were so chosen that the $\bar{y}$ value on a scale which represents an absolute black body by zero and a perfect white body by 100 will be the relative brightness. Thus, instead of using the tristimulus method of color specification, more information is supplied if a color is specified in terms of $\bar{y}$, x, and y.

In a graphical representation the tristimulus values would require a three dimensional coordinate system, whereas the trichromatic coefficients can be plotted in the conventional manner, and the plot is called a chromaticity diagram. From a chromaticity diagram the dominant wave length of a particular color can be determined by extending a line through the coordinates of the measured sample and the illuminant point out to the spectrum point. A numerical specification of purity of the sample can also be obtained by merely determining on the chromaticity diagram the relative distances of the sample point and the corresponding spectrum point from the illuminant point. Figure 2 shows a chromaticity diagram for Illuminant A.

A color specification in terms of brightness $\bar{y}$, trichromatic coefficient x, y, and z, dominant wave length

Chromaticity Diagram for Illuminant A

FIGURE 2



and purity is definitely described in objective terms by the spectral distribution of energy of the illumination being used.

SOLID SOLUTION:

The early work on equilibrium diagrams had made it clear that in many systems the first addition of one component to another did not produce a new phase but resulted in the formation of a homogeneous system which was regarded as a solid solution of one component in the second. These solid solutions which form the end phases in equilibrium diagrams are called primary solid solutions and x-ray investigations have shown that primary solid solutions have the same crystal structure as the parent material.(8)

The solid solution formed is of two types, that of substitutional solid solution, in which the solute atoms replace those of the solvent and, as a result, the two types of atoms are situated on a common lattice. The second type is that of interstitial solid solution. Here the solute atoms fit into the spaces between those of the solvent.

The criteria for the existence of solid solution are as follows:

1. Atomic Size Factor - Since it has been pointed out that a distortion in the lattice takes place, it is

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(8) Hume-Rothery, The Structure of Metals and Alloys, Institute of Metals, Monograph, and Report Series #I

only natural to assume there should be some connection between the atomic diameters of the two components and their tendency to form solid solutions. From experimental evidence, Hume-Rothery, Mabbot, and Channel-Evans,(9)(10) have postulated that when the atomic diameters of the solute and solvent differ by more than 14-15% of that of the solvent, the size factor is unfavorable and the solid solution, if any, is apt to be very restricted. If the sizes are within these limits, the size factor is favorable, and the nearer the sizes, the more favorable are the conditions for solid solution formations.

Solid solutions are not always formed when the size factors are favorable, therefore, it is only a preliminary test to indicate whether two materials are likely to form solid solutions.

2. Crystal Structure - It is not absolutely necessary for the two components to be of the same crystal type to form a solid solution, however, if the crystal structure of the components are different a continuous solid solution is not likely to result. Instead only a limited amount will be obtained depending on which of the two components acts as the solvent.

3. Electro-negative Valency Effect - In general,

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(9) Channel-Evans, Crystal Chem., p. 144, Cambridge Press

(10) Hume-Rothery, Mabbot, and Channel-Evans, Phil. Trans. Roy. Soc., 1934, (A), 233, 1.

the more electro-negative the solute material and the more electro-positive the solvent material (or vice versa) the greater is the tendency for the formation of stable intermediate compounds, which would in turn decrease the chances of solid solution formation.

4. <u>The Relative Valency Effect</u> - It has been experimentally noted by Bernal and other investigators that an element of lower valency will generally dissolve more of one of higher valency than vice versa.

These four factors are all relative and there are exceptions to each of them, and even though most of the experimental work and literature references refer to metallic alloys the reasoning can well be applied to systems such as are being used in this investigation. Since there must be an initial starting point these factors help considerably in that respect.

A solution must consist of more than one component but must be in a single phase. When the solute is a solid, it becomes a problem to determine whether or not there is only one phase present. The best method of attack is that of x-ray diffraction, provided it is crystalline solids with which we are dealing. If a second phase is present in considerable amount, two different x-ray patterns will be simultaneously obtained, superimposed on each other. If no second phase can be found, it may tentatively be assumed that the two original components are in solution. In such a case the x-ray pattern will resemble that of the solute material except that the lattice parameter will be somewhat altered. The higher the concentration of the solute in the solvent the greater will be the change in the lattice parameter.

When it has once been established that the two component systems have only a single phase so that it may be classified as a solid solution, it remains to determine whether the molecules (atoms or ions) of the solute lie between the molecules (atoms or ions) of the solvent or whether they replace them in the lattice. This may be done by comparing the density of the solid solution determined by ordinary physical means, with the density calculated by means of the lattice parameter of the solid solution.(11) If the solid solution is interstitial,

$$D = \frac{n_1 M_1 + n_2 M_2}{V} \times 1.649 \times 10^{-24}$$

where:

n_1 = number of molecules (or atoms) of solvent in the unit of structure of the pure solvent.

n_2 = number of molecules (or atoms) of the solute material in the unit structure calculated from the concentration of the solid solution.

M_1 = molecular weight of the solvent.

M_2 = molecular weight of the solute.

V = volume of the unit cell of the solid solution.

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(11) W. P. Davey, Study of Crystal Structures and Its Application, Ch XVIII, McGraw Hill.

If the solid solution is substitutional,

$$D = \frac{n \times 1.649 \times 10^{-24}}{\left(\frac{a}{M_1} + \frac{b}{M_2}\right) V}$$

where:

a = weight fraction of the solute.

b = weight fraction of the solvent.

n = number of atoms in the unit cell.

V = volume of the unit cell.

COLOR AS A RESULT OF CRYSTAL STRUCTURE:

As has been mentioned, from a physical standpoint the word color is used to refer to the property of preferential absorption of light of one or more wave lengths in the visible spectrum. Of course, this is only arbitrary, since absorption outside the visible spectrum is equally important.(12)

The absorption of light including preferential absorption of particular wave lengths which give rise to color is due to electronic transitions within the atoms. It has been noted by Hume-Rothery that ions with one incomplete shell give no absorption in the visible spectrum and are colorless. Those with two incomplete shells (the transition elements) are the most highly colored and those with three incomplete electron shells, generally the rare earth elements, give absorption bands, but they are not in the visible spectrum. To be able to produce a color in

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(12) A. F. Wells, Structural Inorganic Chem., Oxford Press.

the visible spectrum an ion must be capable of an electronic transition corresponding to the absorption of a quanta of light.

When a particle is held in position by definite constraints, it is capable of vibrating with a definite frequency, and this frequency is determined by the magnitude of the constraints and the mass of the particle.(13) If the constraints are not uniform in all directions, there will, in general, be three frequencies of vibration corresponding to the three constraints of the different axis. When the vibrations are in the order of the frequencies of visible light they cause absorptions which result in a visible color. Thus, the constraints along the axis controls the frequency of vibration which, in turn, controls the color. In general, colored substances have electrons which are least firmly held.

LABORATORY PROCEDURE:

The initial procedure in the problem was to make a literature survey and to classify the transition element oxides, rare earth element oxides, and some refractory oxides as to their crystal structure and ionic radii of the metallic cation.(14)(15)(16)(17)(18) This classification

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(13) G. N. Lewis, The Atom and the Molecules", J. A. Chem. Soc., #38, 762, (1916).

(14) Ester Band, International Taballen, Vol. 2.

was utilized to establish systems in which solid solutions might possibly be obtained. Figure 3 gives a graphical representation of the size of the metallic cation and the crystal system of the oxides used in this investigation.

The proposed method of procedure was to prepare various systems in 10 percent by weight intervals and fire them in an electric kiln in intervals of 100°C from 1000°C to a temperature sufficient to establish solid solution, that is, within a feasible range and 1800°C was arbitrarily chosen as the maximum limit. X-ray diffraction patterns were then to be taken on the sample to determine whether or not a solid solution was present. Unfortunately, the forward reflection patterns taken with the 90° rotation of a North American Phillip X-ray machine was not sensitive enough to detect slight shifts in "d" values; and, as a result, a back reflection camera setup had to be employed to determine any shift in the lattice constants. This procedure was considerably more tedious than the forementioned one, so the method was revised to fire for a color and then determine if a solid solution was present.

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(15) Wycoff, The Structure of Crystals, 2nd Edition, Chem. Catalog Co., 1935

(16) Evans, Crystal Chem., Cambridge Press, p. 170

(17) Stillwell, Crystal Chem., McGraw-Hill Book Company

(18) Handbook of Chem. and Phys., Chem. Rubber Pub. Co.

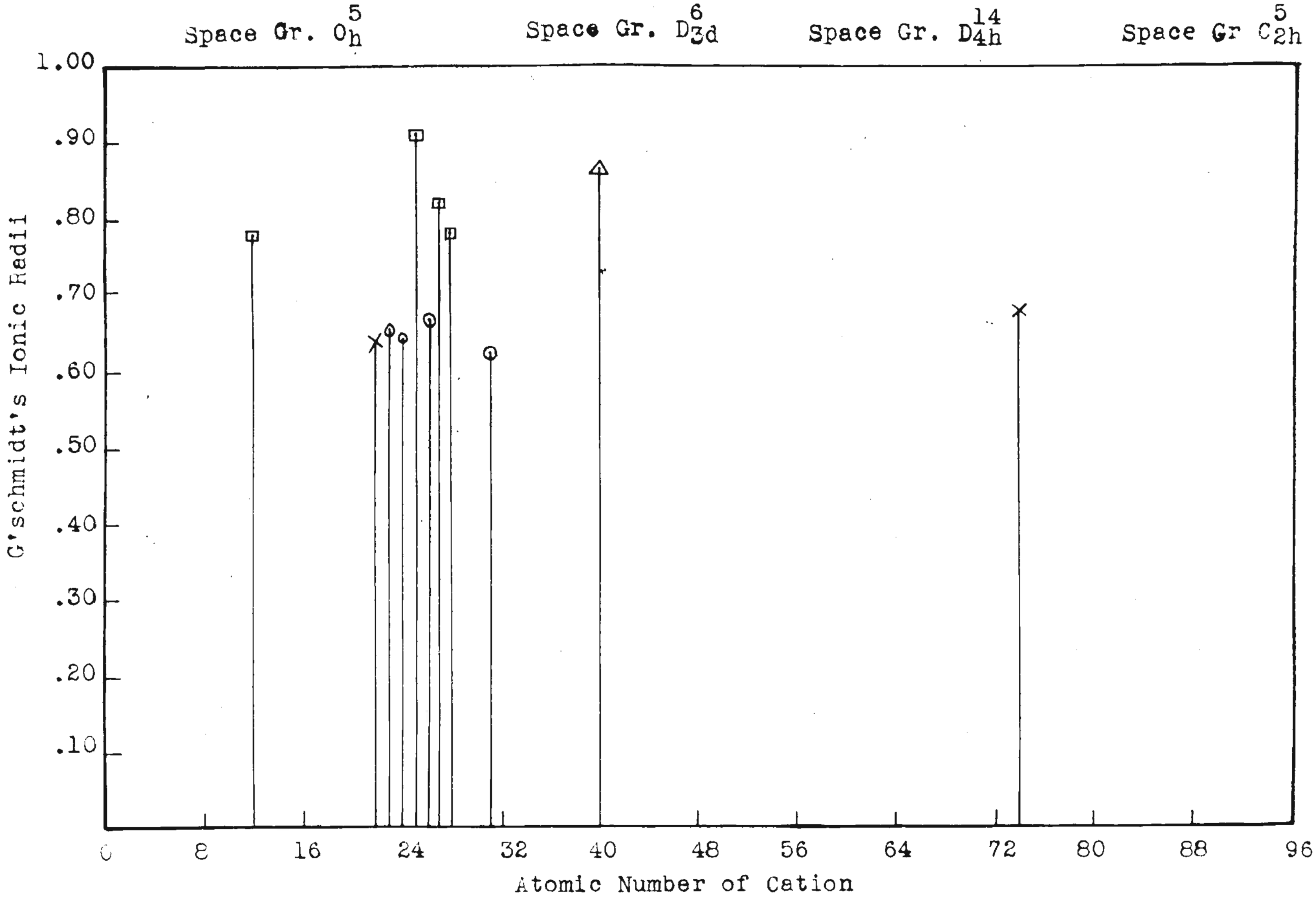
Space Gr. O_h^5
Space Gr. D_{3d}^6
Space Gr. D_{4h}^{14}
Space Gr C_{2h}^5
1.00
.90
.80
.70
.60
.50
.40
.30
.20
.10
G'schmidt's Ionic Radii
0
8
16
24
32
40
48
56
64
72
80
88
96
Atomic Number of Cation

Figure 3

Cohen's least square method of calculation was used in determining the lattice parameter of the samples.(19)

A co-precipitation method of mixing was considered and experimented with, but was discarded due to difficulty in obtaining the compound in the desired form at the correct time. Passerini and Hedvall both had used a co-precipitation mixing method;(20)(21) however, they had used KOH as a precipitating agent, which, in turn, formed KCl which was used as a flux. The third compound was not desired in this investigation and, as a result, the oxides themselves were used to make the samples and they were mixed mechanically and were formed into small pellets from a brass mold.

The x-ray data that will be reported for the systems that showed no color will be only that of a representative sample.

The color data was determined by a General Electric recording spectrophotometer using I.C.I. Illuminant A. (See figure 4). The tristimulus values were obtained by use of a tristimulus integrator,(22) and the trichromatic coefficients,

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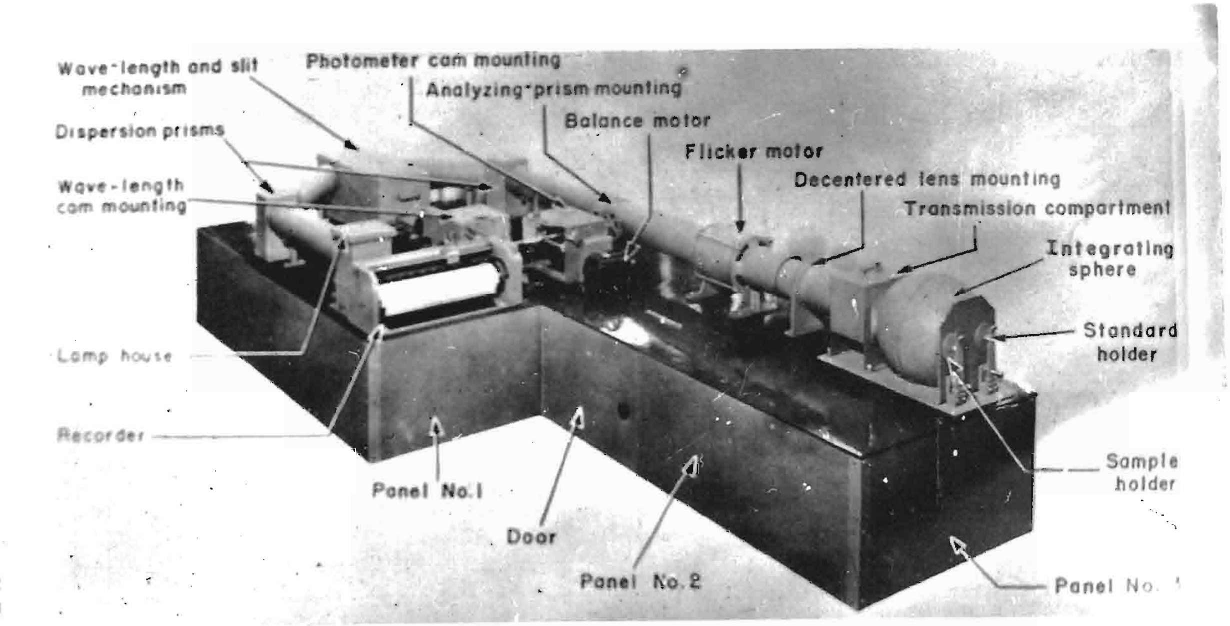
(19) M. U. Cohen, Precision Lattice Constants from X-ray Photographs, Review of Scientific Inst., Vol. 6, pp. 68-74, (1935).

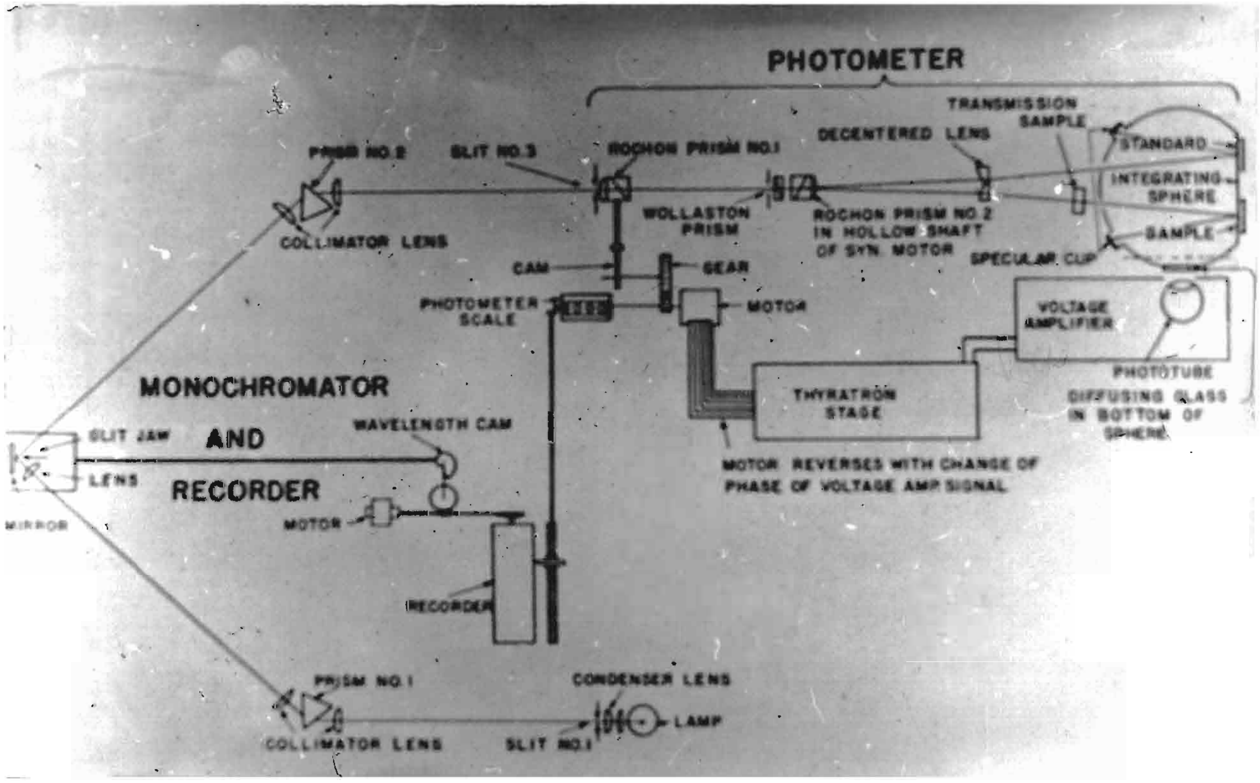
(20) Passerini, Gass. Chem. Italia, Vol. 59, 1929, p. 144

(21) Hedvall, Zeitsch. Anorg. Chem., 1914, p. 296

(22) F. W. Sears, Improved Calculation for Obtaining Tristimulus Values from Spectrophotometric Curves", Jour. Optical Soc. of America, Vol. 29, p. 77, (1939)



G.E. Recording Spectrophotometer



Schematic Diagram of Spectrophotometer
FIGURE 4

dominant wave lengths, purity, and brightness, were calculated in the conventional manner.(23)

The materials used in this study were all chemically pure and of the reagent grade with the exception of the Ga_2O_3. This oxide was prepared from pure Gallium (99.9% pure) by a method used by the Bureau of Standards.(24) This essentially consisted of dissolving the Gallium in acid solution of HNO_3, H_2SO_4 and HCl, then precipitating the $Ga(OH)_3$ and igniting to a constant weight. In the preparation of the oxide 99.5% of the pure Gallium was recovered as the oxide.

DATA:

System NiO-CoO:

The first system prepared was that of NiO-CoO because a continuous solid solution had already been reported.(25) By knowing that a solid solution was present, it was hoped that such a solution could be verified by forward reflection and, too, if any color was developed it could be investigated. In this case the solid solution could be detected by a forward reflection, since the lattice parameters were considerably different (NiO is 4.1717 A°, CoO is 4.24 A°).

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(23) A. C. Hardy, Handbook of Colorimetry, Technological Press, Cambridge, Mass.

(24) Lundell and Hoffman, Bureau of Standards, Atomic Weight of Gallium, RP 838, Jour. of Research National Bureau of Standards, Vol. 15, p. 409, (1935)

(25) Passerini, Gass. Chem. Italia, Vol. 59, p. 144, (1929)

However, it was felt for more accurate work, a forward reflection on the North American Phillip machine would be used for identification purposes only and then back reflection would be used to determine the a_o of the systems, provided a color was obtained. Table 1 gives a sample of the CoO-NiO system. It will be noted in this case the NiO is the solvent material and CoO the solute, and, as a result, the "d" values of the solid solution more closely approaches that of NiO.

TABLE 1

80% NiO + 20% CoO

θ (CuK_{α_1})	d(exp.)	NiO d Values	CoO d Values
39° 24'	1.211	1.203	1.227
39° 30'	1.263	1.258	1.281
31° 15'	1.481	1.474	1.50
21° 36'	2.088	2.08	2.12
18° 36'	2.410	2.40	2.45

System TiO_2 - WO_3:

The TiO_2 (rutile) was prepared from C.P. TiO_2 (anatase) by heating to 1200°C and holding for three hours. The WO_3 was prepared by heating tungstic acid to 1000°C and holding for two hours. The oxides, as such, were then weighed and samples processed as given. A continuous solid solution was not probable with this system, but it was hoped that some color or color modification would take place and possibly a partial solid solution be found. 1300°C was the maximum temperature used with this system and no appreciable change in color was noted. However, there was a gradual gradiation from a brown (90% TiO_2) to a silvery grey (90% WO_3). The samples above 70% WO_3 fluxed down at 1300°C and it can be seen from the x-ray data in table 2 that both materials are definitely present with no apparent crystal structure change. The color gradiation mentioned did not seem significant and was, therefore, not measured.

Systems Cr_2O_3 - V_2O_3; Fe_2O_3 - V_2O_3:

The V_2O_3 could not be obtained as such and an attempt was made to prepare it from V_2O_5. Briscoe says that VCl_3 can be made from V_2O_5 by mixing with concentrated HCl.(26) This procedure was attempted and the VCl_3 was precipitated as $V(OH)_3$ with $NH_4(OH)$. However, when the NH_4Cl salts were burned off, the V_2O_3 was again oxidized back to V_2O_5.

Samples were then prepared using the V_2O_5 as such and they were fired in a strong reducing atmosphere, and, as was expected, the Cr_2O_3 and the Fe_2O_3 were reduced to CrO and FeO respectively. The Fe_2O_3 samples fluxed down around 700°C and the Cr_2O_3 samples fluxed down at about 1000°C. Since the melting point of V_2O_5 is comparatively low, 690°C, and that of V_2O_3 is 1970°C, it can be assumed that very little V_2O_3 was obtained.

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(26) Briscoe, General Chem. for Colleges, Riverside Press, Cambridge, Mass.

TABLE 2

60% WO_3 40% TiO_2

θ (CuK_{α_1})	$d_{(exp.)}$	TiO_2 d Values	WO_3 d Values
11° 36'	3.823	-	3.81
12° 12'	3.637	-	3.65
13° 42'	3.245	3.24	-
14° 22'	3.105	-	3.15
16° 38'	2.685	-	2.65
17° 3'	2.622	-	2.65
18° 3'	2.481	2.49	-
19° 33'	2.296	2.29	-
20° 36'	2.185	2.19	-
22° 00'	2.052	2.05	-
23° 36'	1.920	-	1.92
24° 10'	1.878	1.88	-
25° 0'	1.818	-	1.82
26° 42'	1.711	-	1.70
27° 7'	1.686	1.69	-
27° 54'	1.643	-	1.65
31° 00'	1.492	-	1.49
31° 18'	1.479	1.48	-
31° 54'	1.455	1.449	-
34° 22'	1.362	-	1.389
34° 45'	1.348	1.355	-
38° 15'	1.242	1.245	1.24
41° 0'	1.172	1.70	1.179
42° 54'	1.129	-	1.121

Systems of ZrO_2-NiO; ZrO_2-CoO:

ZrO_2 is an oxide of many modifications depending on the heat treatment. It is monoclinic from room temperature to 1000°C with a_o= 5.21, b_o= 5.26, c_o= 5.37 A°,   = 80°32'. Above 1000°C it is tetragonal with a_o= 5.07, c_o= 5.16 A°, and it can be trigonal or pseudo-hexagonal with prolonged heating at very high temperatures (1900°C).$^{(27)}$ Ruff and Ebert have reported that with concentrations of MgO from 4 to 40 percent by weight, a cubic solid solution is formed.$^{(28)}$ This writer experimented with Ruff and Ebert's idea, but unfortunately was not able to completely form one phase. Samples of ZrO_2 with 4% and 10% MgO were made up and fired to 1400°C. These were then investigated with a petrographic microscope and by x-ray diffraction. From the microscopic analysis one would conclude that there was only one phase present; however, the x-ray showed two distinct phases, but the MgO lines were shifted somewhat. In view of this fact it was not expected to get a continuous solid solution, but the systems were tried hoping that possibly a color modification of some sort would result. The samples were fired in a gas-oxygen furnace to 1800°C. (This temperature was chosen due to the refractoriness of all the oxides). No color resulted whatsoever. The NiO samples remained intact, but the higher cobalt samples fluxed

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(27) Cohn and Tolksdorf, Forms of ZrO_2 Depending on the Heat Treatment, Z. Phy. Chem., 8 (8), pp. 331-56 (1930)

(28) Ruff and Ebert, Ceramic Abstracts, 9 (2), 108, (1930)

down.

Table 3 shows a representative sample of the NiO-ZrO_2 system. The "d" values indicate definitely that there is no solid solution formed between the NiO and ZrO_2. No MgO lines appeared, so it is assumed that with this small percentage it formed a solid solution with the NiO, but not indicating a significant shift to show up in a forward reflection pattern. In any event there was no color modification apparent.

TABLE 3

50% NiO 46% ZrO_2 4% MgO

θ CuK_{α_1}	$d_{(exp.)}$	NiO d Values	ZrO_2 d Values
39° 37'	1.205	1.203	-
37° 36'	1.259	1.258	-
31° 22'	1.477	1.474	-
29° 54'	1.542	-	1.55
27° 36'	1.659	-	1.66
25° 00'	1.819	-	1.81
24° 36'	1.846	-	1.85
21° 40'	2.082	2.08	-
18° 36'	2.410	2.40	-
15° 45'	2.83	-	2.85
14° 6'	3.155	-	3.19

System $MnO-ZrO_2$:

MnO, having a favorable size factor, it was decided to attempt to make provisions to fire it at high temperatures in order to keep it from reverting to the ordinary high temperature form of Manganese, Mn_3O_4.

A small inert atmosphere chamber was cast in two pieces from alumina slip and these were prefired before being used in a run. Considerable difficulty was encountered in the casting of these pieces, since grinding time, casting specific gravity, and percent electrolyte desirable for deflocculation, had to be experimentally determined. Houth has done considerable similar work on alumina castings and his casting data is based on pH and specific gravity.(29) However, at present, he has no data available on the firing of the castings and this is where the most difficulty was encountered in the present work. In the final casting slips that were used for the inert atmosphere chamber the alumina was first dry ground through 100 mesh and then the batch was made up to a specific gravity of 2.3-2.4, and 2% HCl added as a deflocculant. The pieces were cast and allowed to air dry for 3-4 days. The dryer was originally used after the first day, but invariably cracking would occur upon firing. They were then fired to 1200°C on a 15-18 hour schedule and allowed to cool very slowly to room temperature. Such

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(29) W. E. Houth, Jr., Slip Casting of Aluminum Oxide, PhD thesis, MIT, Camb., Mass. Reported at 1949 meeting of A.C.S. and soon to be published in Jour. Amer. Cer. Soc.

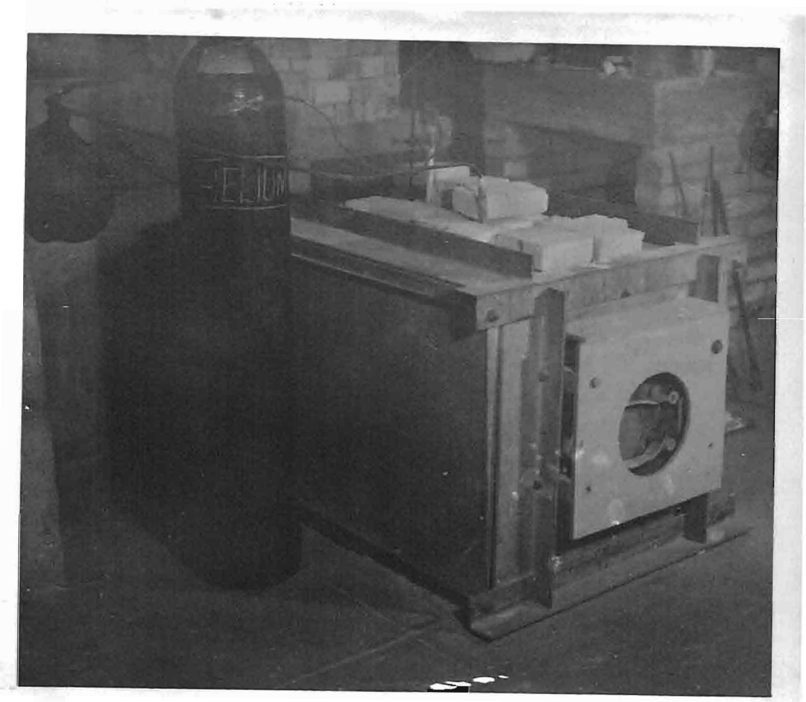
precautions are necessary in solid and thick castings because the heat shock resistance of alumina is very low. Figure 5 shows the assembled firing apparatus, figure 7 the modification used when $MnCO_3$ was used to obtain the MnO, and figure 6 shows the modification used when MnO, as such, was used.

Two seperate runs were made. In both cases the temperature was taken to 1300°C. In the first, $MnCO_3$ was used as a source of MnO and Nitrogen was used as the inert gas. However, oxidation occurred due to the seal breaking in the cooling operation. X-ray data in table 4 indicates clearly the presence of Mn_3O_4. No color modification occurred and all the samples were black. Values for the x-ray pattern of Zirconium Nitrate were also checked. This was a possibility since oxidation did occur. The data shows that one line checks very closely; however, this is the only indication.

TABLE 4

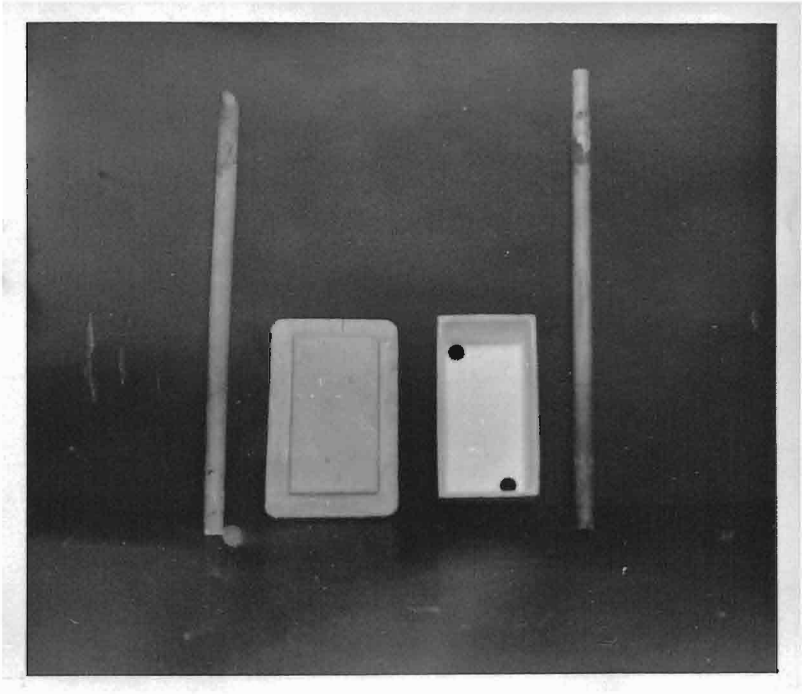
40% MnO 60% ZrO_2 Nitrogen Atmosphere

θ CuK_{α_1}	$d_{exp.}$	Mn_3O_4 d Values	ZrO_2 d Values
14° 6'	3.15	3.11	3.19
15° 44'	2.84	2.87	2.85
16° 16'	2.74	2.75	-
18° 54'	2.36	-	2.34
20° 42'	2.17	-	2.17 ($Zr(NO_3)_4$)
25° 00'	1.819	-	1.81
27° 16'	1.673	-	1.66
32° 30'	1.431	1.438	1.426

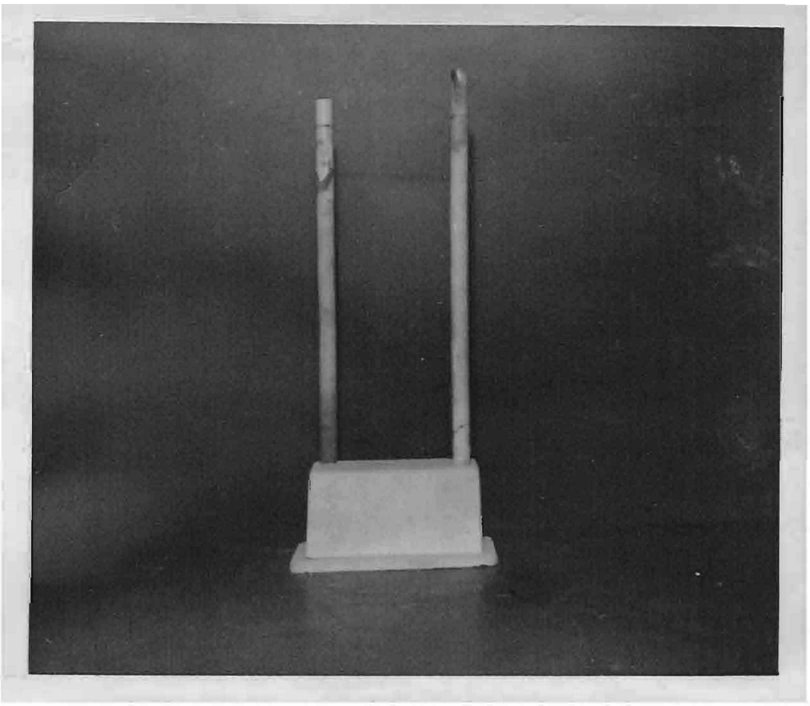


Firing Arrangement, with Inert Chamber
FIGURE 5

MnO Modification of Inert Gas Chamber
FIGURE 6



$MnCO_3$ Modification Disessembled



Inert Gas Chamber, $MnCO_3$ Modification
FIGURE 7

In the second run two types of samples were made up, one set with MnO (as such) and ZrO_2, and a second set with MnO-ZrO_2 and 4 percent MgO. In this run Helium was used as an inert gas to eliminate the possibility of forming nitrides.

Oxidation also occurred in this run due to a faulty chamber. The seal was good until the maximum temperature of 1300°C was reached and then apparently the chamber cracked as indicated by the pressure giving way suddenly. When this happened the samples were immediately drawn, hoping to cool them suddenly and possibly get oxidation only on the surface. This was not the case, however, and the samples were all oxidized and again Mn_3O_4 formed, resulting in a black color. No difference was noted in the samples with or without the MgO. Table 5 gives the x-ray data of the system fired in the Helium atmosphere.

Systems NiO-MgO and CoO-MgO:

The two systems that have given positive colors are that of NiO-MgO and CoO-MgO.(30)(31)(32) The solid solutions for these systems have been reported, (see figure 6), but the color information, as far as can be ascertained, has not been reported to date.

The NiO-MgO system was prepared and fired to 1600°C.

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(30) Hedvall, Zeitsch Anorg. Chem., 1914, Vol. 86, p. 296, 1918, Vol. 103, p. 249

(31) Passerini, Gass. Chem. Italia, Vol. 59, 1929, p. 144

(32) H. v. Warenberg and E. Prophet, Z. Anorg. u. allgem. Chem., Vol. 208, p. 379, (1932)

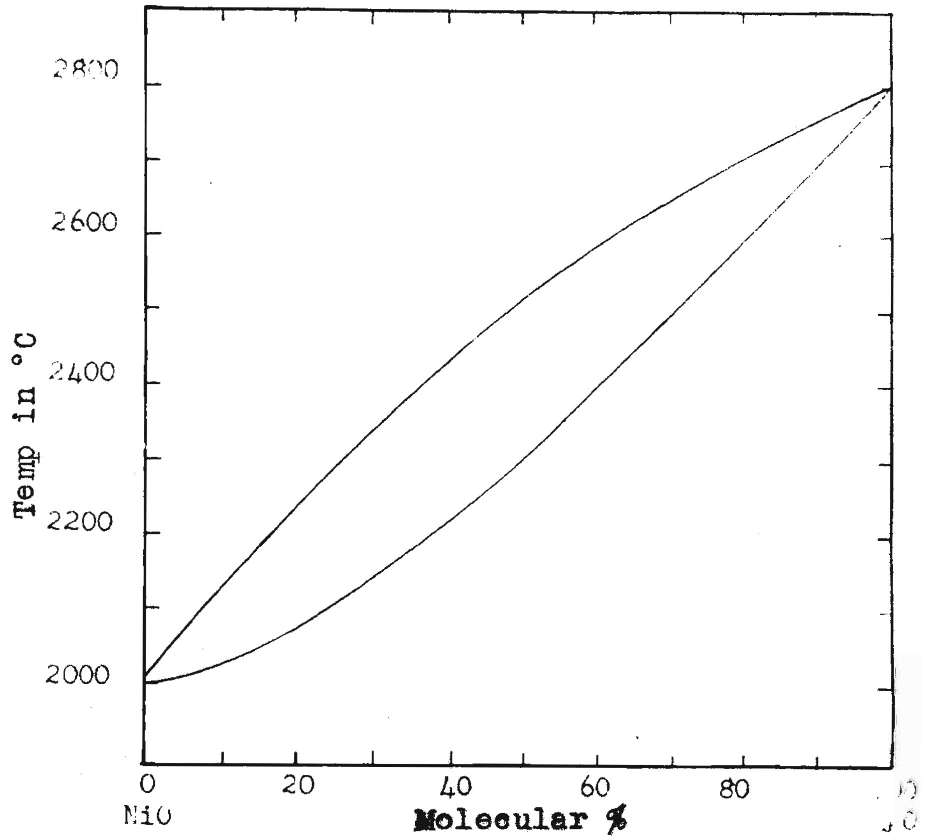
TABLE 5

40% MnO 60% ZrO_2

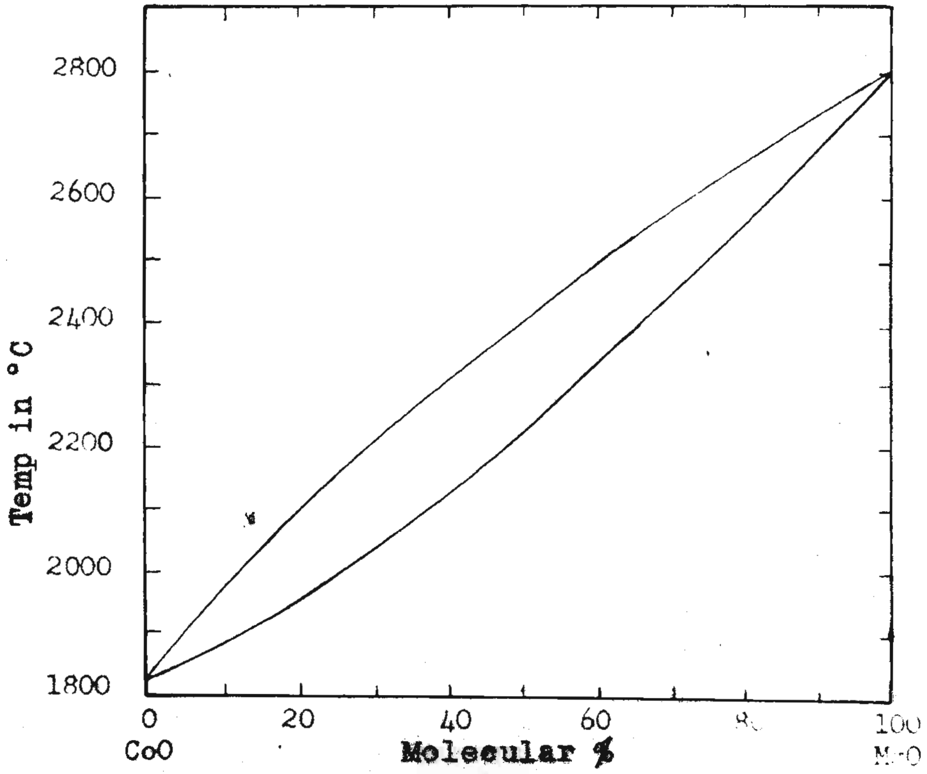
Helium Atmosphere

θ (CuK_α)	$d_{(exp.)}$	Mn_3O_4 d Values	ZrO_2 d Values
14° 7'	3.18	-	3.19
15° 45'	2.84	-	2.85
16° 18'	2.738	2.75	-
17° 12'	2.578	2.56	-
18° 54'	2.373	2.36	-
20° 24'	2.205	-	2.21
25° 6'	1.812	-	1.81
27° 18'	1.676	-	1.66
27° 45'	1.650	1.64	-
28° 6'	1.632	1.64	1.62
32° 30'	1.430	1.438	1.426

SYSTEM NiO - MgO
Phase Diagram



SYSTEM CoO - MgO
Phase Diagram



H.v. Warenberg and E. Prophet, Z. anorg. u. allgem. Chem., V208, 379,(1932)

FIGURE 7a

This high firing temperature was used because the maximum color intensity with the low percentages of NiO was obtained in this range, and it was also hoped that a temperature in this range would improve the stability of the stain as a colorant.

The CoO-MgO system was fired to 1300°C. Since its first color appeared around 1100°C, it was also hoped that the additional 200 degrees would improve its stability, as well as intensify the color.

For the x-ray data of the samples a flat cassette, back reflection type camera was used and for the calculations of the a_o of each of the components of the NiO-MgO system, unfiltered copper radiation and Cohen's method of calculations (33) were used.

For the CoO-MgO system, iron radiation was used, but Cohen's method was not applicable because only one doublet could be obtained on the pattern (as will be explained later). As a result, a_o of this system had to be calculated from the experimental "d" values and the known radius of the camera.

It is known that the basis for all precision measurements is by the use of back reflections or x-rays that have been diffracted through angles of 2θ nearly equal to 180°. For

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(33) M. U. Cohen, Precision Lattice Constants from X-ray Powder Photographs, Review of Scientific Instruments, Vol. 6, pp. 68-74, (1935)

values of θ near 90° the values of sin θ can be calculated to a high precision even if the angle θ is known only roughly.

Cohen states that there are two types of errors, random and systematic. The random errors will average out, but the systematic errors are shrinkage of the film, radius of the camera, sample displacement, and adsorption.

For a Debye camera (the flat, back reflection cassette is essentially a Debye camera) Cohen has shown that the systematic errors give values of $\sin^2\theta$ in error by the amount $D \sin^2 2\theta$, where D is different from film to film but is constant for any one film.

For cubic crystals the formula for each reflection when no error is present is:

$$A_o (h^2 + k^2 + l^2) = \sin^2\theta \quad \text{where } A_o = \frac{\lambda^2}{4 a_o^2}$$

When errors are present the formula becomes:

$$A_o(h^2 + k^2 + l^2) + D\sin^2 2\theta = \sin^2\theta$$

Therefore, when two or more reflections are given, it is possible to calculate both A_o and D, by solving simultaneous equations.

By the method of least squares, the following equations were set up and solved for A_o and D:

$$A_o \sum\alpha^2 + D\sum\alpha\delta = \sum\alpha \sin^2\theta$$

$$A_o \sum\alpha\delta + D\sum\delta^2 = \sum\delta \sin^2\theta$$

where:

$$\alpha = (h^2 + k^2 + l^2)$$

$$\delta = 10 \times \sin^2 2\theta$$

The accurate a_o was then calculated from A_o, and D indicates the amount of deviation.

Table 3 gives a sample calculation using C. P. MgO and figures 7 and 8 show a reproduction of the x-ray patterns.

The density of a representative sample of the system, 50% NiO-50% MgO, was determined by means of a pycnometer in accordance with A.S.T.M. designation C 135-47 and was found to be 4.385. The density was also determined by means of the formulas given in the introduction,(34) and was found to be 4.65 for that of substitutional type solid solution and for the interstital type to be 5.12. It is expected that the calculated density will be a little higher because closed pores in the material would cause the specific gravity as determined by the pycnometer to be somewhat lower. Since the atomic radii of the two percent materials are so nearly alike it may be assumed that the solid solution is of the substitutional type.

Table 7 gives the complete x-ray data of the NiO-MgO system and figure 9 indicates graphically the relationship, and the approach to Vegard's linear additivity law.(35)

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(34) Davey, Study of Crystal Structure and Its Applications, Chapter XVIII, McGraw-Hill

(35) Vegard, L., Ztsch. Physik, Vol. 5, p. 17, (1921)

TABLE 6

Calculation of a_o for MgO

Cu Radiation

Line	Tan 2 ϕ	2 ϕ	2 ∅	θ	Sin 2θ	Sin θ	Plane
α_2	.70906	35°20'22"	144°39'38"	72°19'49"	.57841	.95278	333
α_1	.73684	36°23'6"	143°36'54"	71°48'27"	.59321	.94998	333
α_2	1.2865	52°8'30"	127°51'30"	63°55'45"	.78953	.89825	422
α_1	1.3158	52°45'53"	127°14'7"	63°37'4"	.79617	.89585	422

Line	α	$\sin^2 2\theta$	$\sin^2\theta$	$\sin^2\theta$	α^2	δ^2	$\alpha\delta$	$\sin^2\theta$	$\sin^2\theta$
α_2	27	.33456	.90780	.90312	729	11.193	90.331	24.389	3.021
α_1	27	.35190	.90246	.90246	729	12.383	95.012	24.366	3.176
α_2	24	.62336	.80685	.80285	576	38.357	149.606	19.267	5.004
α_1	24	.63389	.80255	.80255	576	40.181	152.133	19.261	5.087
					2610	102.615	487.081	87.283	16.288

Normal Equations:

$$A_o \Sigma\alpha^2 + D\Sigma\alpha\delta = \Sigma\alpha \sin^2\theta$$

$$A_o \Sigma\alpha\delta + D\Sigma\delta^2 = \Sigma\delta \sin^2\theta$$

$$A_o (2610) + D(487.08) = 87.283$$

$$A_o (487.08) + D(102.146) = 16288$$

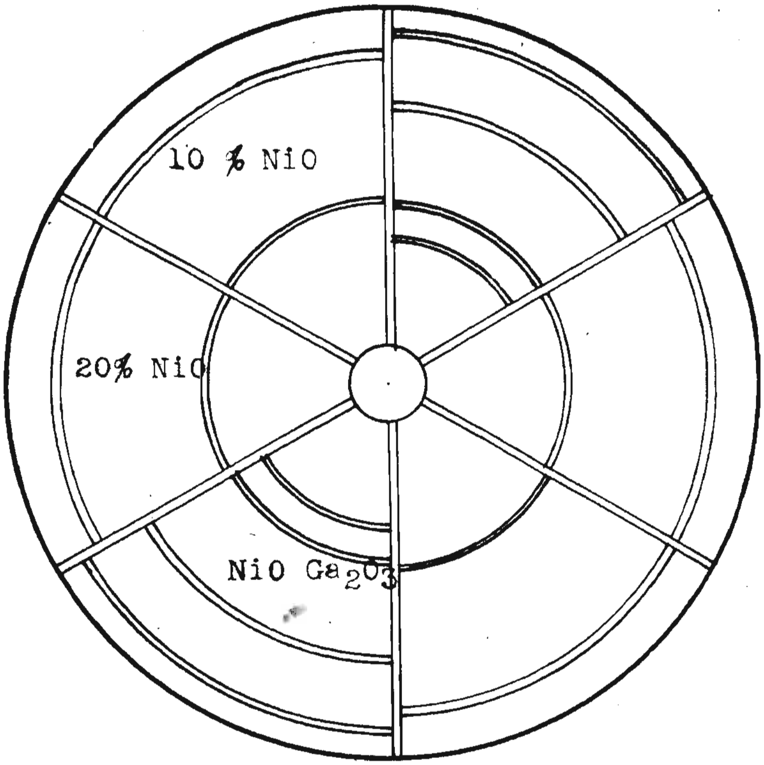
A_o = .0334456

D = -00002

a_o = 4.2032_7

a_o^3 = 74.261

Literature Reference a_o = 4.20



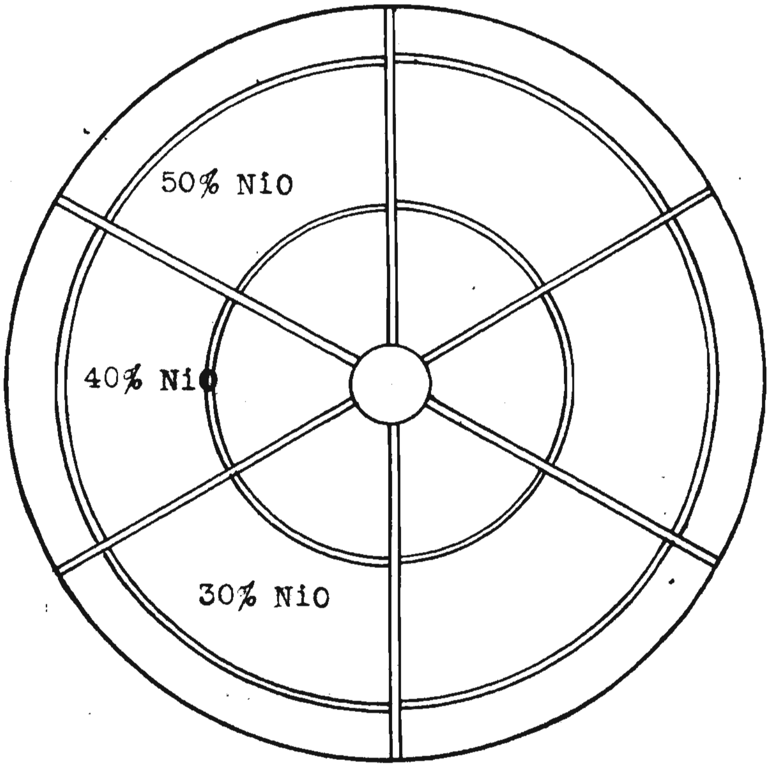


FIGURE 8
X-ray Patterns of NiO-MgO, NiO Ga_2O_3

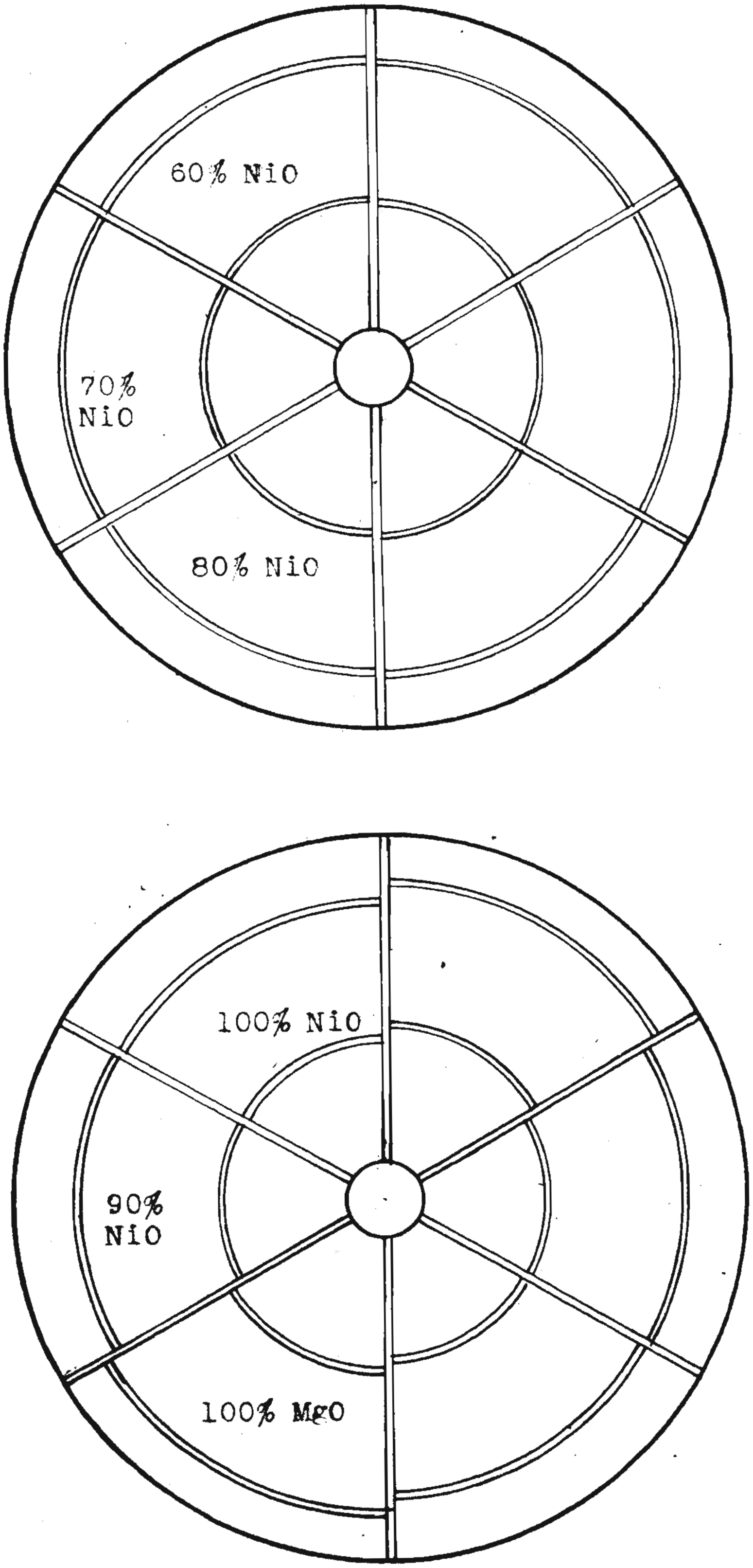


FIGURE 8a

X-ray Patterns of NiO-MgO Components

TABLE 7

X-Ray Data of NiO-MgO

Wt. % NiO	Molecular % NiO (36)	a_o	D	a_o^3
10	5.8%	4.2021	-.00005	74.2005
20	12.0	-	-	-
30	19.5	4.1959	-.00006	73.8774
40	27.1	4.1922	-.0002	73.6731
50	36	4.1900	-.00011	73.5631
60	46	4.1869	-.00004	73.4000
70	57	4.1827	-.00017	73.1720
80	69	4.1800	-.00011	73.0395
90	84	4.1753	-.00010	72.7930
100	100	4.1717	-.00018	72.5619

The percent reflectance in the visible range of wave lengths for each of the components of the system NiO-MgO was made on powdered samples ground through 100 mesh. The percent variation in dominant wave length between different preparations of the same sample varied from .5% - 1%. The effect of particle size was investigated in a representative sample of each system and it was found that the variation was within the limits of the sample preparation error. The color data is completely tabulated in table 8 and the

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(36) D. S. Eppelsheimer and J. E. Reynolds, A Momograph for Converting Weight Percent to Atomic Percent, Missouri School of Mines and Metallurgy Bulletin #72, June, 1948.

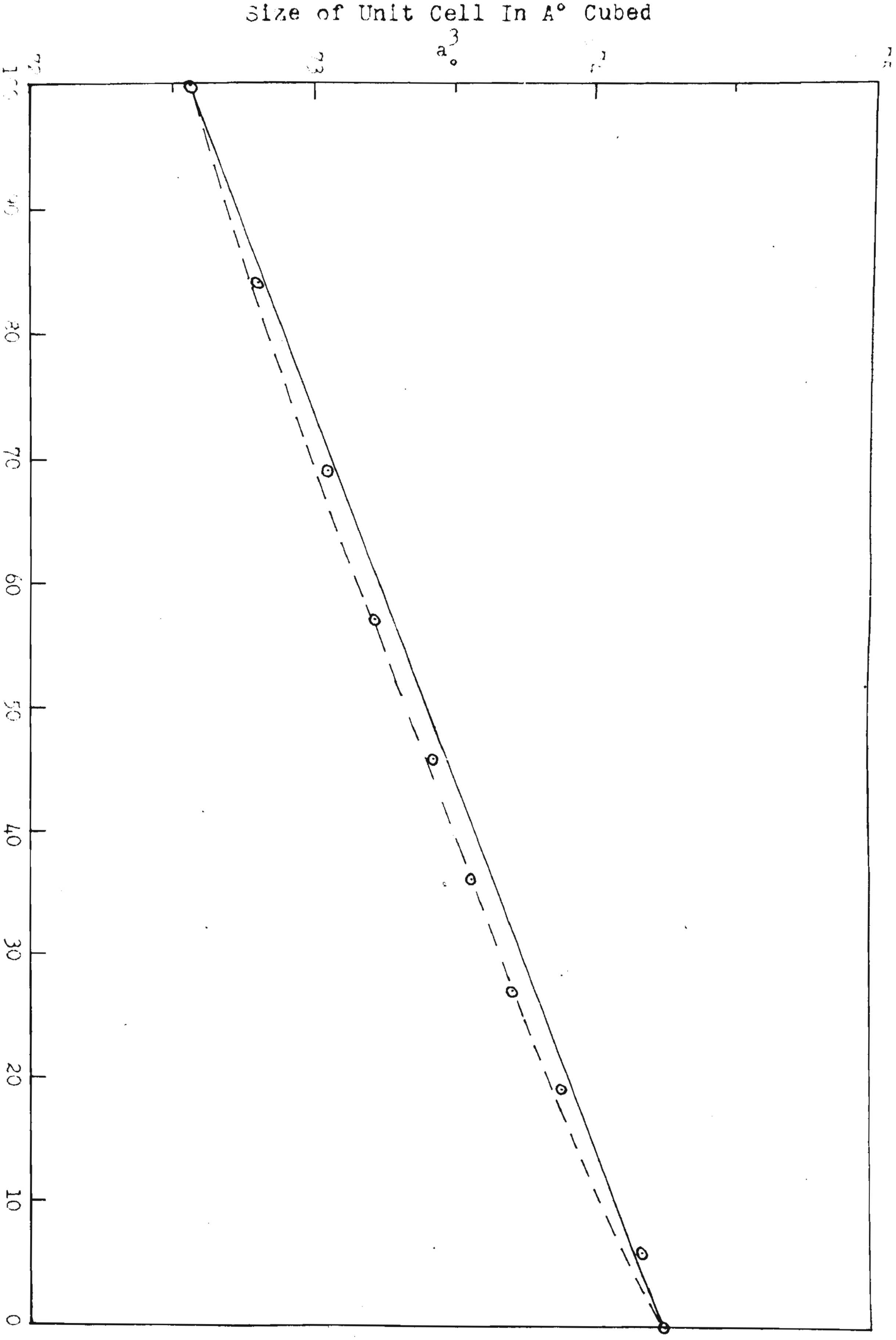
Size of Unit Cell In A° Cubed
a_o^3
100
90
80
70
60
50
40
30
20
10
0
Molecular % OF NiO

FIGURE 9

reflectance curves are shown in figure 10.

In the CoO-MgO system, as has been stated, Cohen's method of a_o determination could not be used. Instead the values were calculated from Bragg's law, $n = 2d\ \text{Sin}\theta$, and from the fundamental equation of the cubic system,

$$d^2 = \frac{a_o^2}{h^2 + k^2 + l^2}$$

Using this method, the random and systematic errors were not eliminated. However, an appreciable shift in the lattice constants are noted. Table 9 gives the tabulated x-ray results and figure 11 shows them graphically. The x-ray patterns are reproduced in figures 12 and 13. The calculated densities from the a_o values of the 50% CoO-50% MgO system are 4.59 for the substitutional type and 5.05 for the interstital type. The true density determined by means of a pycnometer is 4.50, thus indicating that the solid solution is of the substitutional type.

The percent reflectance of each of the components of the system was made on powdered samples ground through 100 mesh, in exactly the same manner as the NiO-MgO system was treated. The color data is tabulated in table 10 and the reflectance curves are shown in figure 14.

TABLE 8

Color Data for MgO-N10 System

I.C.I. Illuminant A

% MgO	Tristimulus Values $\bar{x}$	$\bar{y}$	$\bar{z}$	Trichromatic Coefficients x	y	z	Excitation Purity	Relative Brightness	Dominant Wave Length
10%	19.22	17.26	4.68	.467	.419	.114	22%	17.26%	584
20	23.83	21.63	5.17	.471	.427	.102	29	21.63	582
30	29.07	27.16	6.16	.466	.435	.099	31	27.16	578
40	37.56	35.29	8.09	.464	.436	.100	33	35.29	579
50	42.17	39.79	9.33	.462	.436	.102	29	39.79	577
60	50.99	48.39	11.99	.458	.434	.108	25	48.39	577
70	55.43	52.56	13.67	.456	.432	.112	21	52.56	577
80	60.00	56.79	15.06	.455	.430	.114	20	56.79	576
90	71.93	67.12	19.66	.453	.432	.124	13	67.12	575
60% -325	52.93	49.10	12.62	.460	.432	.102	24	49.10	578

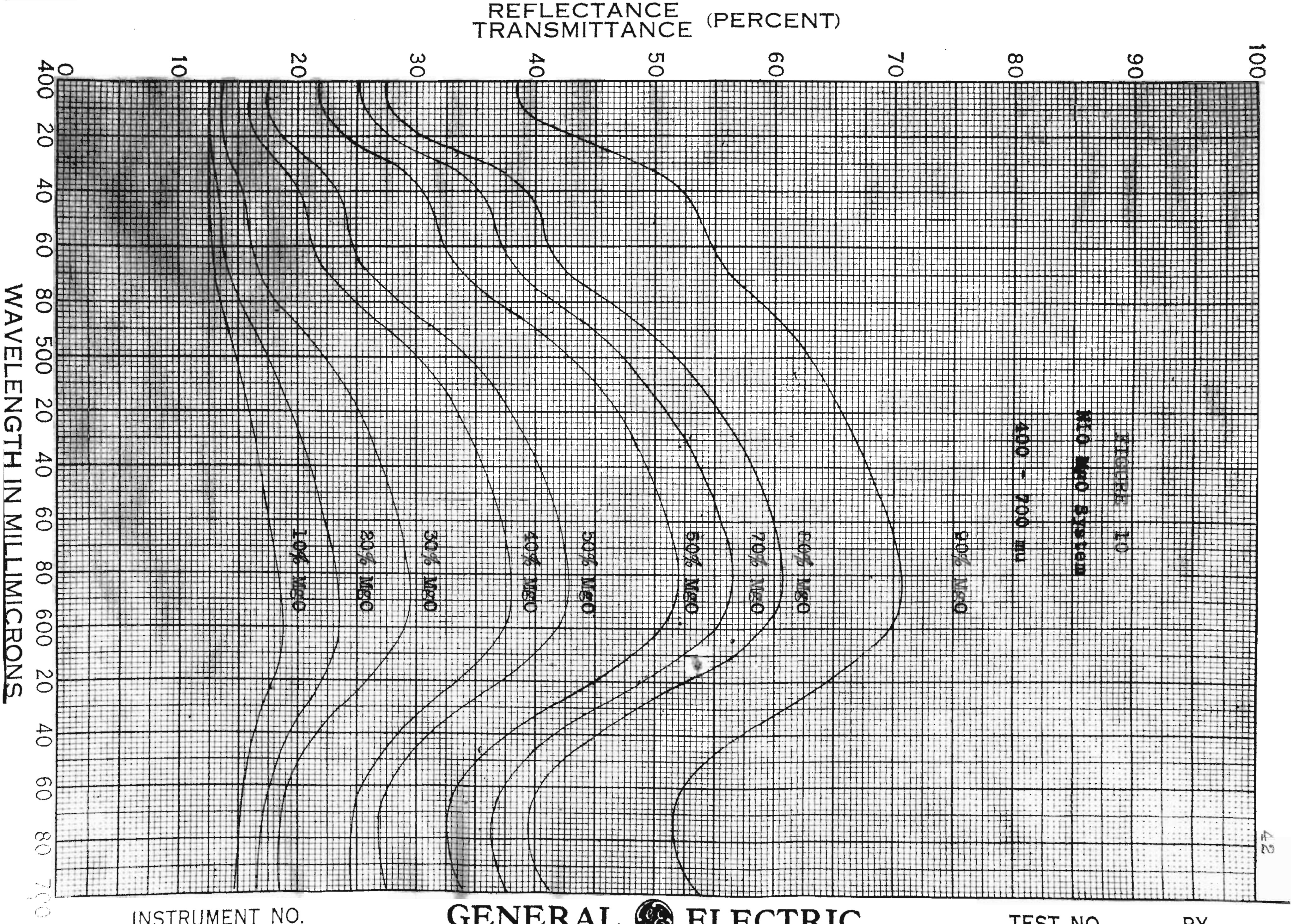

FIGURE 10
NiO MgO System
400 - 700 mu

INSTRUMENT NO.

GENERAL ELECTRIC

TEST NO.............BY..........

TABLE 9

X-Ray Data of CoO-MgO System

Fe Radiation

Wt. % CoO	Molecular % CoO	a_o	a_o^3
10	5.8%	4.2014	74.1611
20	12	4.2032	74.2564
30	19.5	4.2066	74.4652
40	27.1	4.2099	74.6110
50	36	4.2159	74.9326
60	46	4.2201	75.1554
70	57	4.2251	75.4243
80	69	4.2305	75.7170
90	84	4.2398	76.2126

Systems Ga_2O_3-Cr_2O_3 and Ga_2O_3-Fe_2O_3:

The Gallium oxide was prepared as indicated on page 19 and these systems were compounded in three intervals up to a maximum of 33 1/3% Ga_2O_3. The samples were fired to 1200°C, 1300°C, and 1400°C with no resulting color. Forward reflection x-ray patterns show clearly the "d" values of Cr_2O_3, Ga_2O_3, and Fe_2O_3. There is, however, a slight but irregular shift in the 33 1/3% mixtures which may indicate a solid solution; however, no color resulted except that of the characteristic Cr_2O_3 and Fe_2O_3. Therefore, no back reflection work was completed on these samples. Tables 11 and 12 give the x-ray data for

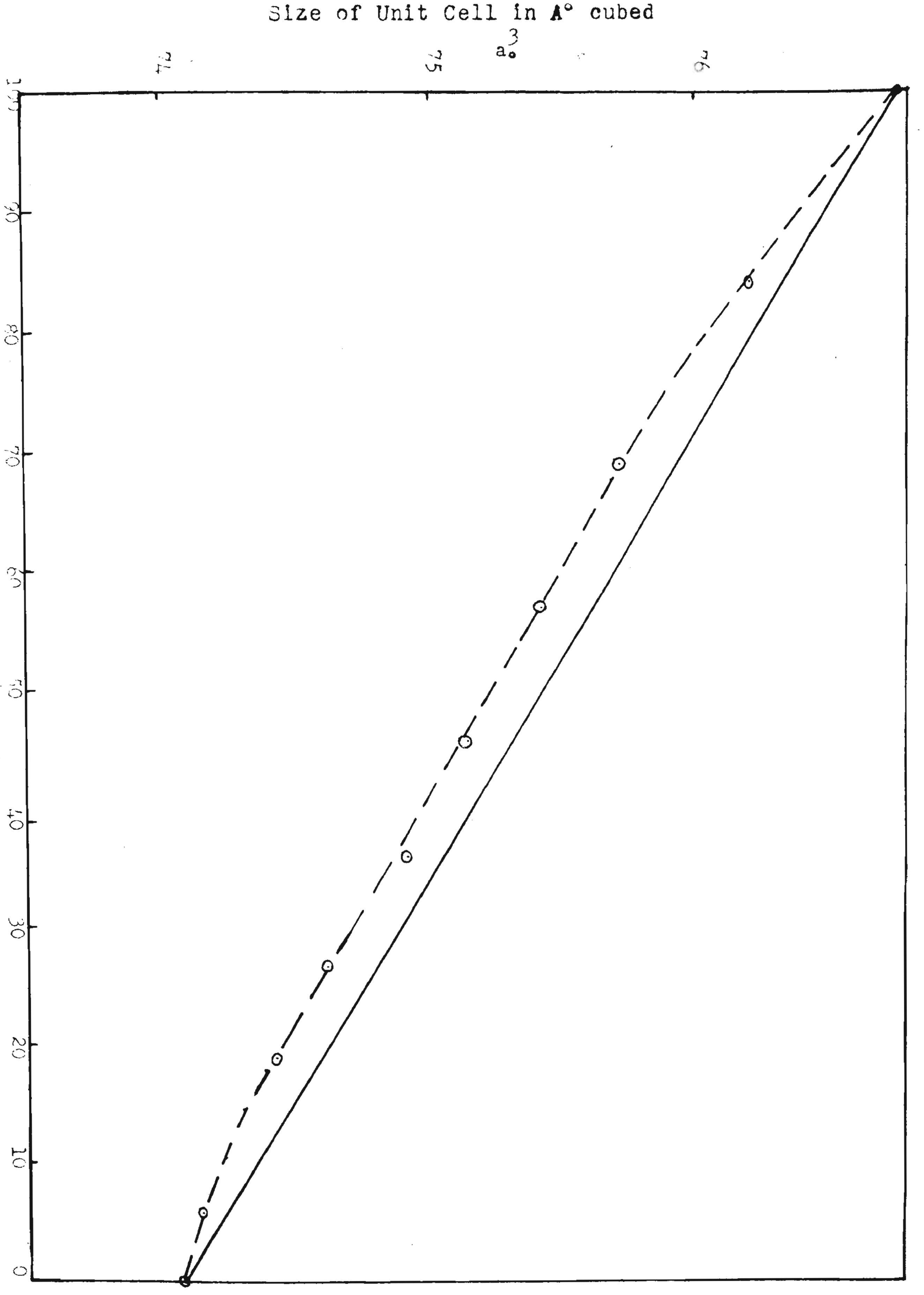
Size of Unit Cell in A° cubed
a_0^3
74
75
76
0
10
20
30
40
50
60
70
80
90
100
Molecular % OF CoO

FIGURE 11

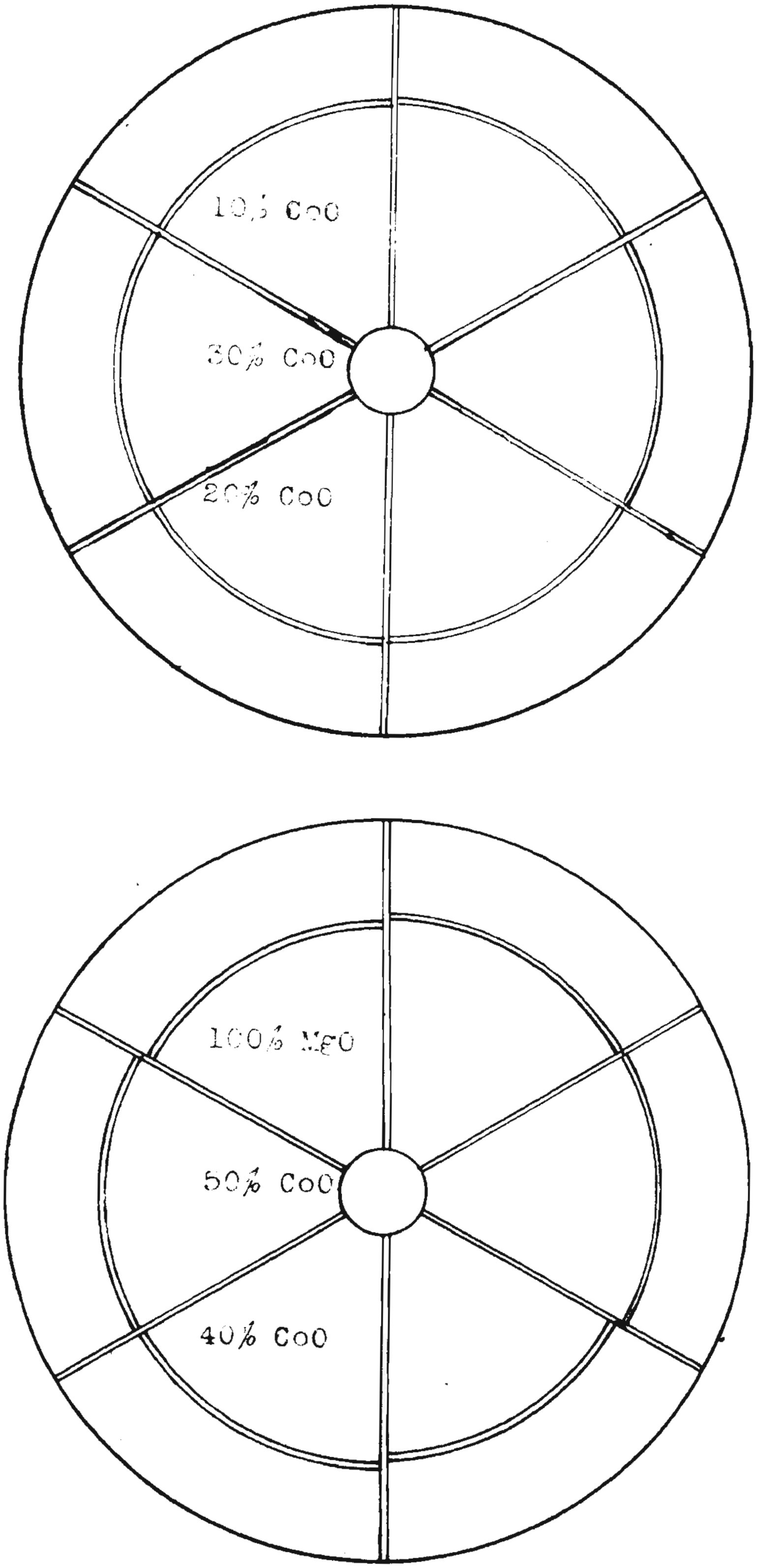

FIGURE 12

Xray Patterns of CoO-MgO, MgO

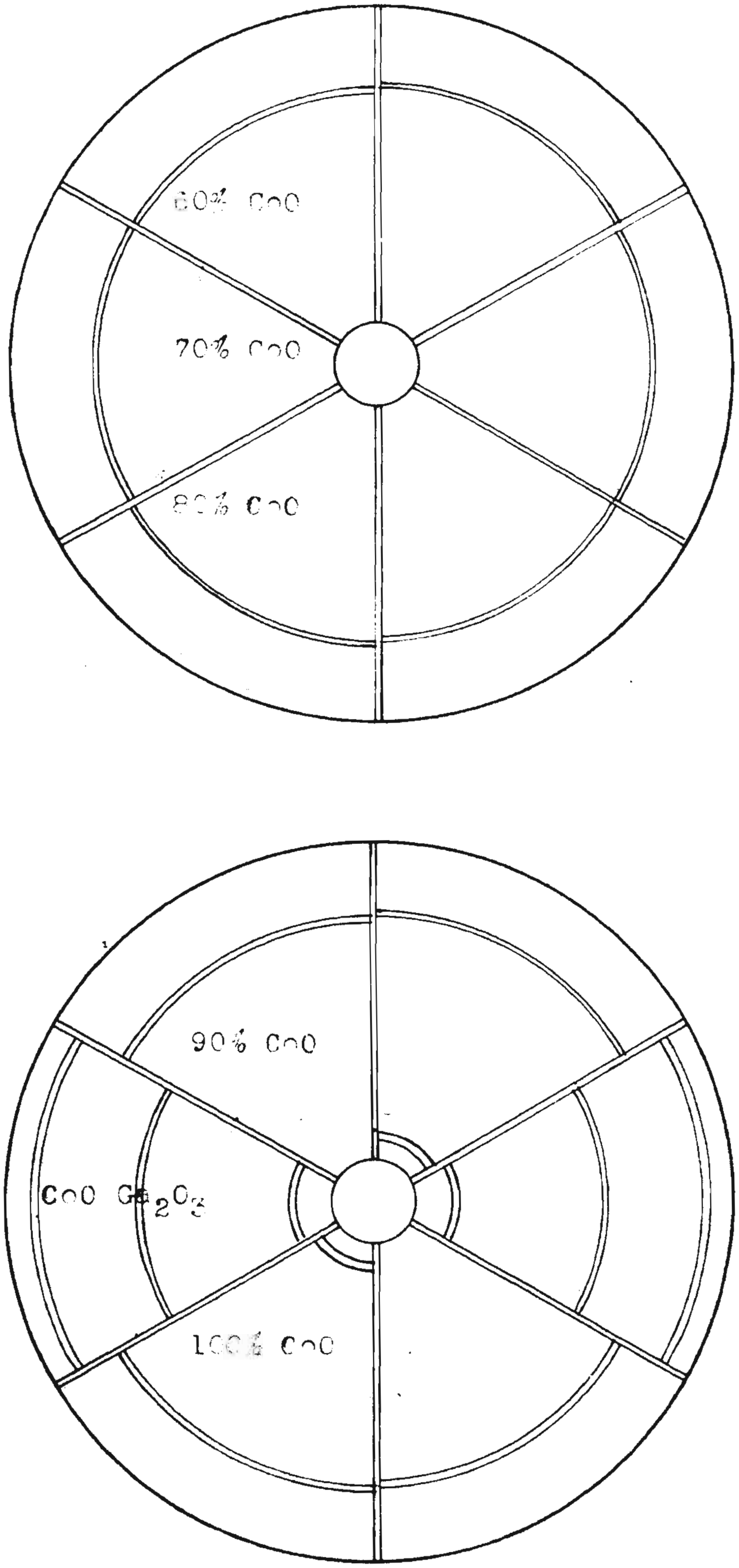

FIGURE 13
X-ray Patterns Of CoO-MgO, CoO Ga$_2$O$_3$

TABLE 10

Color Data for CoO-MgO System

I.C.I. Illuminant A

% MgO	Tristimulus Values			Trichromatic Coefficients			Excitation Purity	Relative Brightness	Dominant Wave Length
	x	y	z	x	y	z			
10%	14.64	12.99	4.35	.458	.406	.136	5%	12.99%	598
20	18.52	15.63	4.90	.474	.400	.125	15	15.63	605
30	23.17	19.26	5.73	.481	.400	.119	19	19.26	599
40	28.99	23.76	7.04	.485	.397	.118	19	23.76	605
50	38.55	31.59	9.54	.484	.396	.120	18	31.59	606
60	48.47	39.83	12.40	.481	.396	.123	15	39.83	609
70	60.37	50.73	16.21	.474	.398	.127	12	50.73	608
80	67.43	57.56	17.03	.474	.405	.120	15	57.56	599
90	78.78	68.86	23.08	.461	.403	.135	8	68.86	601
60% -325	49.39	41.56	12.94	.475	.400	.126	15	41.56	608

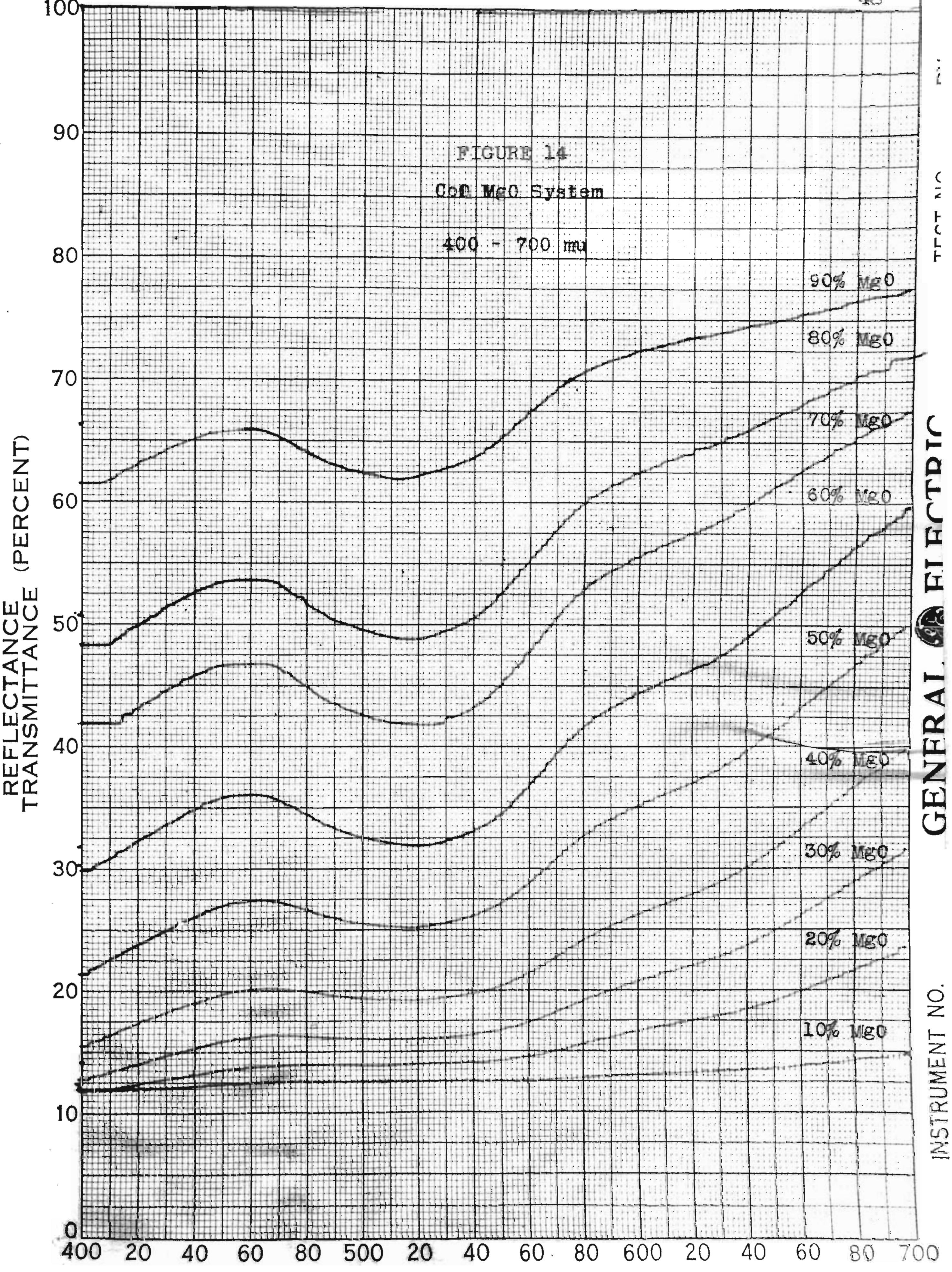

FIGURE 14

CoO MgO System

400 - 700 mu

the forward reflection of a representative sample of these systems. Table 13 gives the "d" values for Ga_2O_3 up to $\theta = 45°$ and figure 15 shows the x-ray pattern.

Since no color resulted with these systems, it was decided to attempt to make a spinel with Gallium oxide and the bivalent oxides NiO and CoO.

The term spinel denotes a compound which has the formula $RO \cdot R_2O_3$ and which possesses the perfect symmetry of the isometric crystal system and crystallizes in the O_h^7 type crystal.(37)(38) They are analogous in structure to the original spinel $MgO \cdot Al_2O_3$. The Magnesium may be replaced by many other bivalent metals and the aluminum by trivalent ones. Some spinels occur in nature, but these are generally impure isomorphous mixtures of different spinels. Artificial spinels can be made by heating the oxides with a mineralizer, such as borax, or even without, provided a high enough temperature is attained.(39) In general, these compounds are refractory and are, therefore, very important in that respect. They are also considered to be relatively resistant to solution by both basic and acid slags.

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(37) J. W. Mellor, Modern Inorganic Chemistry, p. 636, Longmans Green and Co., London, (1916)

(38) Wycoff, The Structure of Crystals, 2nd Edition, Chem. Catalog Co., 1935

(39) Fritz Ephraim, Inorganic Chem., edited by Thorne and Roberts, Interscience

TABLE 11

66.6% Fe_2O_3 33.4% Ga_2O_3

θ CuK_{α_1}	$d_{(exp.)}$	Fe_2O_3 d Values	Ga_2O_3
32° 12'	1.443	1.453	1.438
31° 22'	1.477	1.485	1.480
27° 18'	1.676	1.69	1.678
24° 54'	1.826	1.84	1.836
18° 3'	2.481	2.51	-
16° 48'	2.659	-	2.675
12° 15'	3.62	3.68	3.66

TABLE 12

66.6% Cr_2O_3 33.4% Ga_2O_3

θ CuK_{α_1}	$d_{(exp.)}$	Cr_2O_3 d Values	Ga_2O_3 d Values
12° 20'	3.59	3.62	-
16° 50'	2.654	2.67	2.675
18° 10'	2.463	2.47	-
20° 45'	2.169	2.17	-
25° 9'	1.809	1.81	1.805
27° 30'	1.664	1.67	1.678
29° 12'	1.575	1.58	1.561
31° 42'	1.462	1.465	1.462
32° 30'	1.430	1.432	1.438
36° 42'	1.286	1.294	1.282
38° 18'	1.240	1.236	-

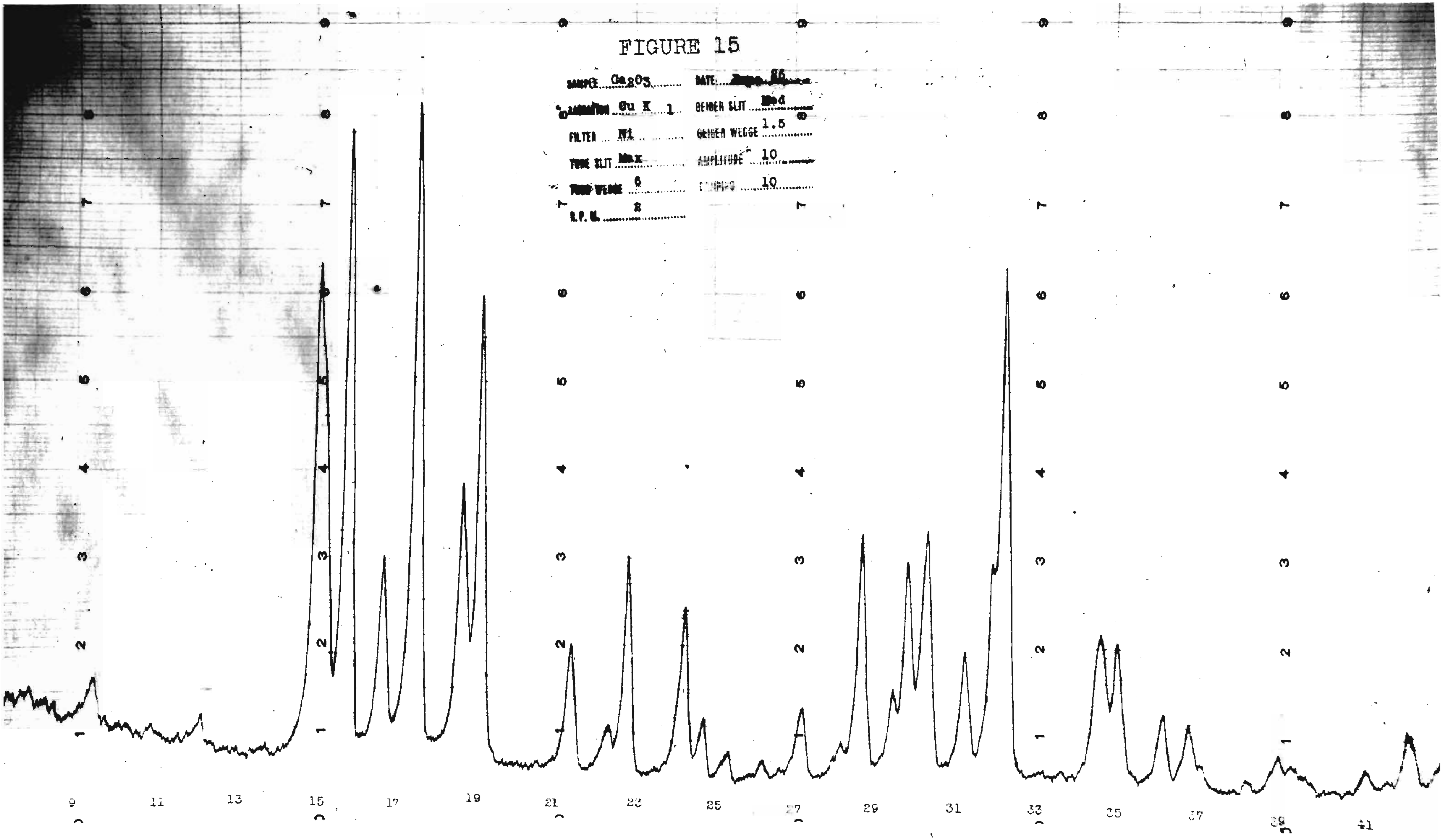
TABLE 13

d Values for Ga_2O_3

θ CuK$_{\alpha_1}$	Ga_2O_3 d Values	θ CuK$_{\alpha_1}$	Ga_2O_3 d Values
9° 27'	4.684	27°15'	1.678
12° 6'	3.667	28°44'	1.598
15° 6'	2.950	29°30'	1.561
15° 50'	2.817	29°52'	1.561
16° 42'	2.675	30°20'	1.522
17° 30'	2.542	31°17'	1.480
18° 42'	2.397	32°18'	1.438
19° 12'	2.337	34°38'	1.352
21° 24'	2.106	35°4'	1.337
22° 21'	2.021	36°8'	1.303
22° 50'	1.980	36°45'	1.282
24° 18'	1.867	38°58'	1.222
24° 45'	1.836	41°00'	1.172
25° 12'	1.805	42°1'	1.148
26° 15'	1.738	42°46'	1.132

FIGURE 15

SAMPLE Ga₂O₃
RADIATION Cu K 1
FILTER Ni
TUBE SLIT Max
TUBE WEDGE 6
R.P.M. 8
DATE [illegible]
GEIGER SLIT Med
GEIGER WEDGE 1.5
AMPLITUDE 10
[illegible] 10



Thenard's blue ($CoO \cdot Al_2O_3$) is a very stable and effective colorant and a similar green spinel is obtained from $NiO \cdot Al_2O_3$. Since the properties of Ga_2O_3 and Al_2O_3 are so similar, it was believed that similar spinels would result.

The first samples that were made were not the true weight percentages of the oxides, but, instead, an excess of the bivalent oxide was used due to the lack of Ga_2O_3. The samples were then fired, first to 1200°C with no resulting color, then to 1400°C. The latter firing resulted in a faint green for the Nickel Spinel and a dark blue for the Cobalt Spinel. Preliminary x-ray patterns and calculations of the lattice constants gave very good indication of the formation of a true spinel.

The theoretical compositions of the proposed spinels were then compounded and the samples fired to 1525°C and held for two hours. The resulting compounds gave a good green color for the nickel spinel and a royal blue for the cobalt spinel. The reflectance curves are shown in figures 16 and 17, and the color data given in table 14.

Back reflection patterns of the compounds were taken and they are reproduced in figures 7 and 13. The lattice parameter of the compounds were calculated by Cohen's method and the complete data is given in tables 15 and 16.

The synthetic spinels were ground through 100 mesh

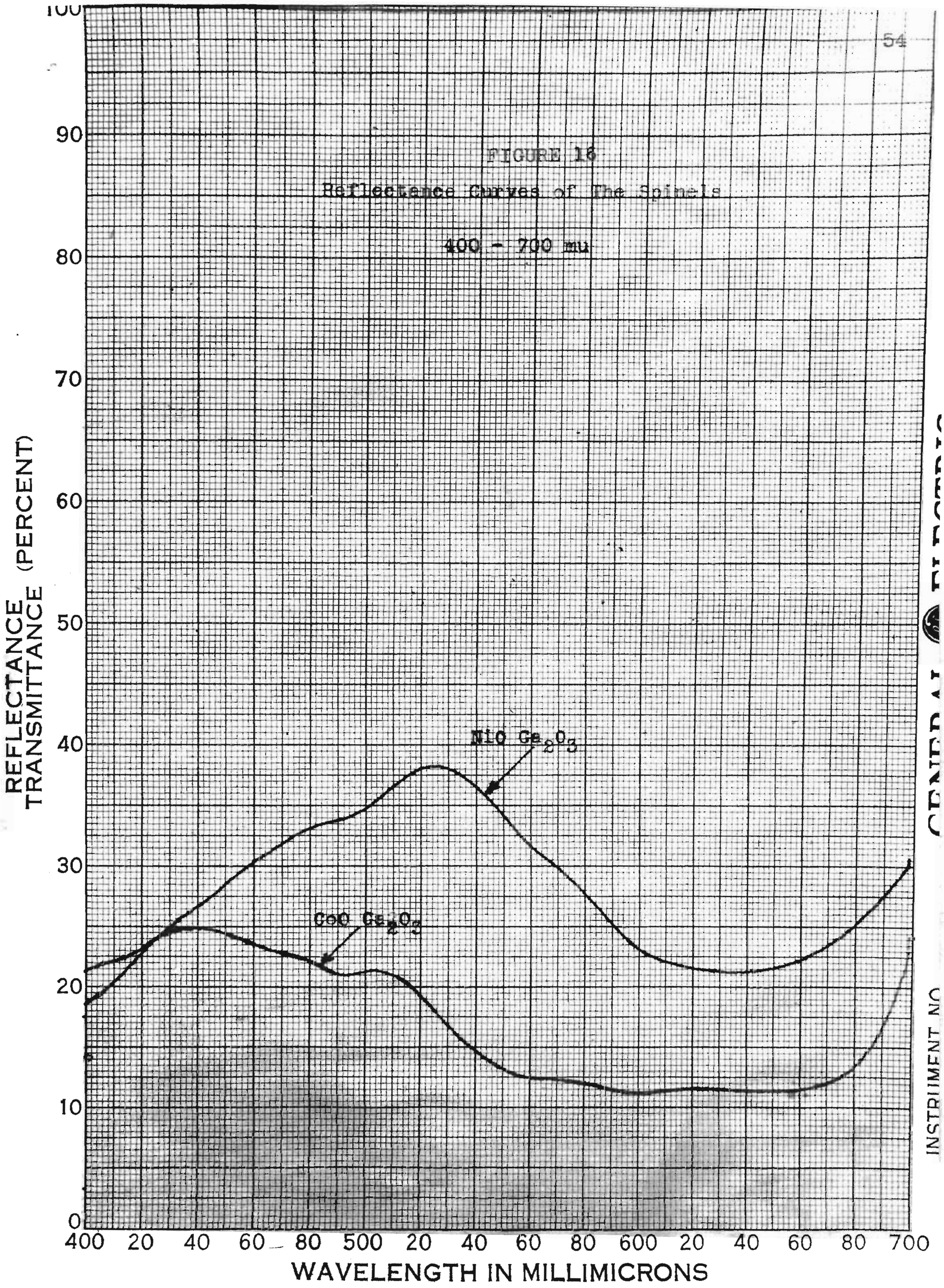


FIGURE 16

Reflectance Curves of The Spinels

400 - 700 mu

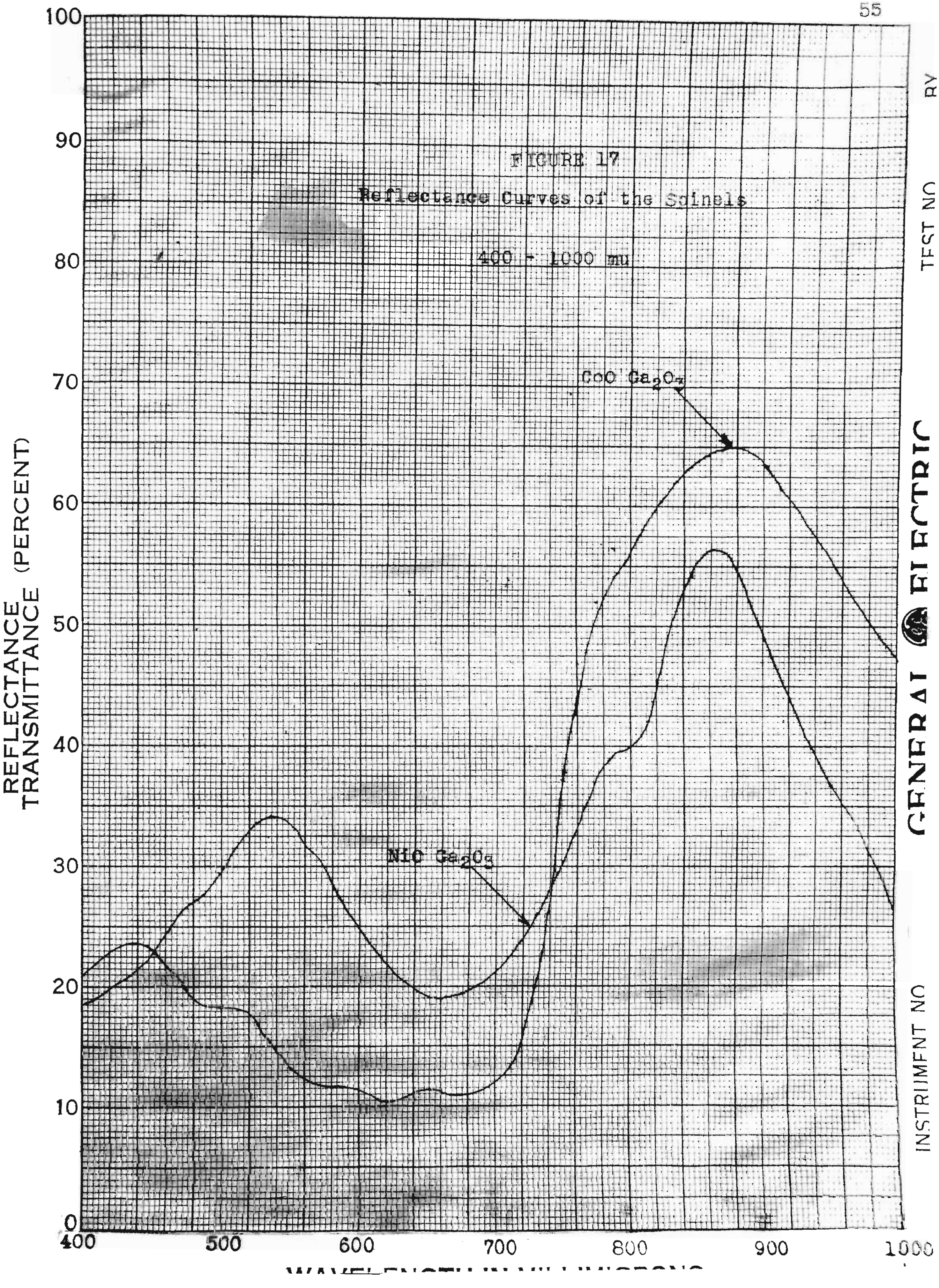


FIGURE 17

Reflectance Curves of the Spinels

400 - 1000 mu

TABLE 4

Color Data For Powdered Samples, Glasses, and Enamels

Composition	Tristimulus Values $\bar{x}$	 $\bar{y}$	 $\bar{z}$	Trichromatic Coefficients x	 y	 z	Excitation Purity	Relative Brightness	D. Wave Length
NiO Ga_2O_3	28.15	29.69	10.80	.410	.433	.157	9%	29.69%	505
CoO Ga_2O_3	14.20	13.83	8.28	.391	.381	.228	15%	13.83%	487
CoO Al_2O_3	12.99	10.37	6.79	.431	.343	.225	18%	10.37%	575c
NiO Al_2O_3	20.87	20.73	8.78	.414	.412	.174	8%	20.73%	498
Soda Lime Silica Glasses									
CoO Alone	3.62	3.20	15.63	.161	.143	.696	85%	3.2%	476
60 MgO 40 CoO	4.65	4.47	16.30	.183	.176	.641	77%	4.47%	477
CoO Ga_2O_3	12.41	13.62	17.98	.282	.309	.409	45%	13.62%	484
NiO Alone	28.03	24.53	6.23	.477	.417	.106	19%	24.53%	586
60 MgO 40 NiO	51.25	45.63	13.95	.463	.412	.124	15%	45.63%	586
NiO Ga_2O_3	52.83	47.09	13.89	.464	.414	.122	15%	47.09%	585
Enamels									
60 MgO 40 CoO	64.07	58.46	25.17	.434	.396	.170	5%	58.46%	480
CoO Ga_2O_3	67.14	61.26	25.76	.436	.397	.167	5%	61.26%	479
40 NiO 60 MgO	87.43	78.93	24.79	.457	.413	.130	21%	78.93%	588
NiO Ga_2O_3	86.55	78.56	25.20	.455	.413	.132	10%	78.56%	583

TABLE 15

Calculation of a_o for NiO Ga_2O_3, Cu Radiation

Line	Plane		θ	$\mathrm{Sin}^2 2\theta$	$\mathrm{Sin}^2\theta$	^{2}	^{2}		$\mathrm{Sin}^2\theta$	$\mathrm{Sin}^2\theta$
α_2	773	107	75°9' 14"	.24540	.93434	11449	6.022	262.579	99.481	2.282
α_1	773	107	74°35'34"	.26242	.92941	11449	6.886	280.789	98.377	2.439
α_2	862	104	72°23'10"	.33273	.90844	10816	11.071	346.039	94.012	3.008
α_1	862	104	71°53'21"	.34918	.90336	10816	12.192	363.142	93.949	3.154
α_2	844	96	66°13'18"	.54200	.83743	9216	29.376	520.320	79.997	4.517
α_1	844	96	65°57'55"	.55348	.83142	9216	30.634	531.337	79.816	4.602
α_2	931	91	63°2' 8"	.65333	.79440	8281	42.684	594.533	71.934	5.165
α_1	931	91	62°44'57"	.66282	.79034	8281	43.954	603.170	71.921	5.239
						79524	182.799	3501.909	689.487	30.404

$$A_o \sum \alpha^2 + D \sum \alpha\delta = \sum \alpha \ \mathrm{Sin}^2\theta$$

$$A_o \sum \alpha\delta + D \sum \delta^2 = \sum \delta \ \mathrm{Sin}^2\theta$$

$$A_o \ 79524 + D \ 3501.909 = 689.487$$

$$A_o \ 3501.909 + D \ 182.799 = 30.404$$

A_o = .0086062, a_o = 8.2559, D = −.00014

TABLE 16

Calculation of a_o of CoO Ga$_2$O$_3$, Fe Radiation

Line	Plane	α	θ	$\sin^2 2\theta$	$\sin^2\theta$	α^2	δ^2	$\alpha\delta$	$\sin^2\theta$	$\sin^2\theta$
α_2	660	72	81°39'	.08258	.97891	5184	.6819	59.454	70.198	.8051
α_1	660	72	80°30'37"	.09872	.97468	5184	.9748	71.079	70.177	.9617
α_2	800	64	69°00'23"	.44752	.87165	4096	20.0274	286.413	55.561	3.8851
α_1	800	64	68°43'10"	.45749	.86829	4096	20.9297	292.794	55.570	3.9723
α_2	355	59	63°46'11"	.62872	.80465	3481	39.5311	370.955	47.474	5.0387
α_1	355	59	63°31'	.63728	.80113	3481	40.6109	375.988	47.267	5.1054
						25522	122.7555	1456.682	346.247	19.7683

$$A_o\sum\alpha^2 + D\sum\alpha\delta = \sum\alpha\sin^2\theta$$

$$A_o\sum\alpha\delta + D\sum\delta^2 = \sum\delta\sin^2\theta$$

$$A_o\ 25{,}522 + D\ 1456.682 = 346.247$$

$$A_o\ 1456.682 + D\ 122.755 = 19.768$$

$$A_o = .013558$$

$$a_o = 8.2966_7$$

$$D = +.00015$$

and their true specific gravities determined by means of pycnometer measurements. The two densities were then computed from these figures.

With the knowledge that eight spinel molecules are associated in the unit cell, the theoretical densities may be computed from the formula:(40)

$$P = \frac{nM}{a_o^3}$$

where:

P = density of the compound

n = number of molecules in the lattice

a_o = unit cell dimension

M = the absolute mass of the molecule = 1.649×10^{-24} of the molecular weight

This calculated density represents the maximum theoretical density of the spinels and should be greater than the values which are obtained experimentally, since the latter determinations involve any voids and inclusions which may be present in the crystalline material.

The calculated densities are as follows:

$CoO\ Ga_2O_3 = 6.06$

$NiO\ Ga_2O_3 = 6.14$

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(40) Parmelee, Badger, Ballam, A Study of a Group of Typical Spinels, University of Illinois Bulletin, Vol. 29, #84, June, 1932

The experimental densities and specific gravities are as follows:

	Specific Gravity	Density
CoO Ga_2O_3	5.98	5.90
NiO Ga_2O_3	6.09	6.06

THE STABILITY OF THE STAINS IN GLASS BATCHES:

Representative samples were selected from the CoO-MgO system and NiO-MgO system, as well as those from the true spinels. Ground through 100 mesh, these were put into a pure B_2O_3 glass batch in the amount of .1% and fired to 850°C. The glasses that resulted showed the stains in very pronounced streaks and small globules indicating that they were not soluble at this temperature. The stains were then ground through 325 mesh and inserted into similar batches. With the increased surface area of this particle size, it was believed that the stains would become thoroughly disseminated throughout the glass. This, however, was a failure. Even by refining the glass at the pouring temperature for two hours, the streaks and globules were still present.

The same stains were then put into a soda-lime-silica glass of the following batch composition:

Potters Flint	57.50%
$CaCO_3$	7.54
Na_2CO_3	23.70
Na_2SO_4	4.70
$NaNO_3$	3.64

NaCl	.64%
Cryolite	3.04
Lamp Black	.30
Colorant	.10

Stains ground through 100 mesh were not used because it seemed more probable that the 325 mesh would give much more contact area. The pouring temperature of this glass is about 1425°C and the refining time is approximately one hour.

Additional glasses were also made containing the same percent of cobalt and nickel oxide as did those of the solid solution. This was to allow a comparison to be made between the glasses, as far as the colorant was concerned. The transmission curves from 400-700 mu and 400-1000 mu are shown in figures 18, 19, 20, and 21 and the color data is given in table 14.

The same stains were also put into an enamel batch having a composition as follows:

<u>Frit</u>

Feldspar	25.0%
Borax	25.5
Quartz	21.0
Soda Ash	3.0
Soda Niter	3.5
Cryolite	14.0
Zinc Oxide	5.0
Antimony Oxide	3.0

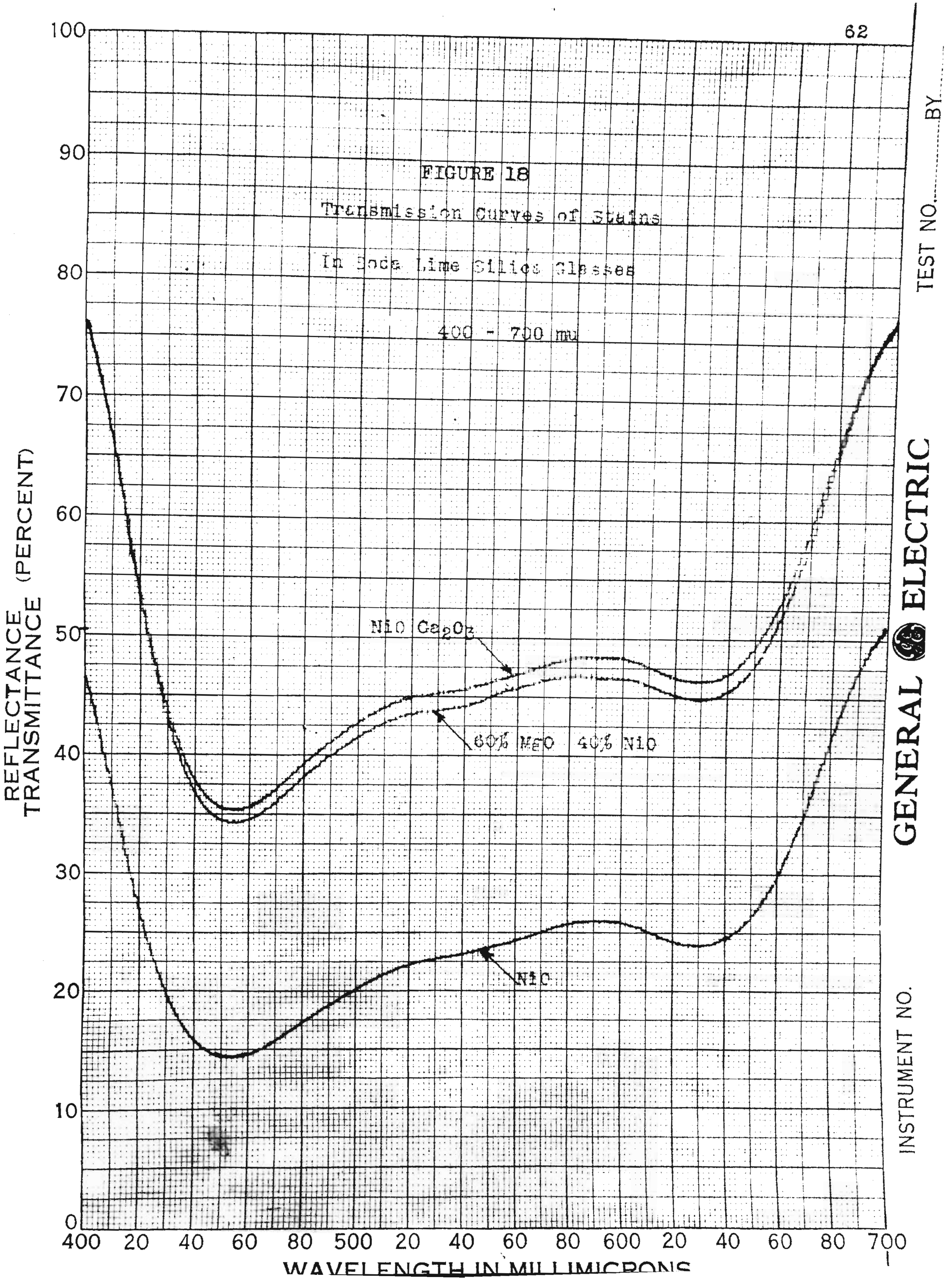

FIGURE 18

Transmission Curves of Stains

In Soda Lime Silica Glasses

400 - 700 mu

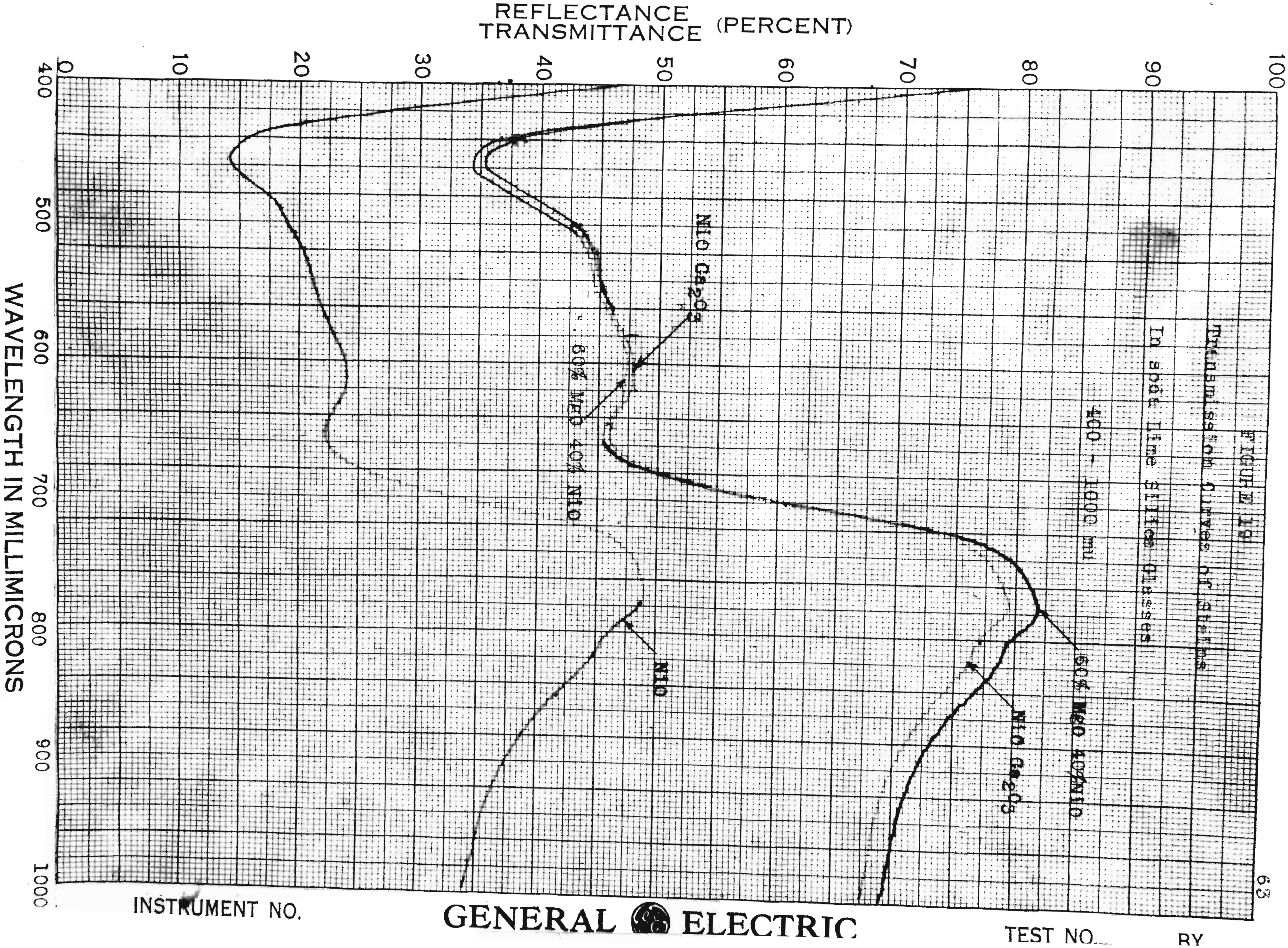

FIGURE 19

Transmission Curves of Stains

In soda lime silica Glasses

400 - 1000 mu

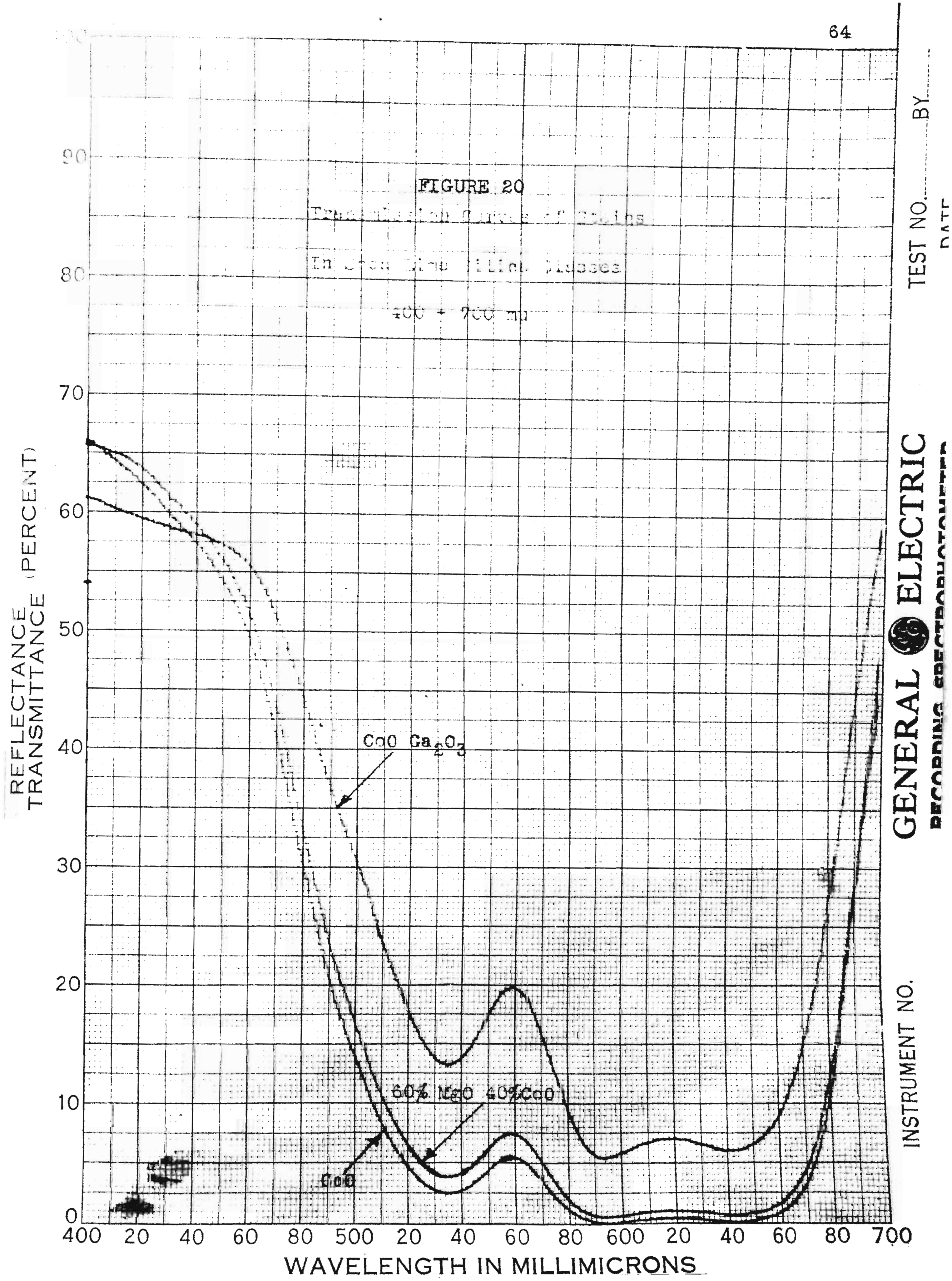

FIGURE 20

Transmission Curves of Stains

In Soda Lime Silica Glasses

400 - 700 mu

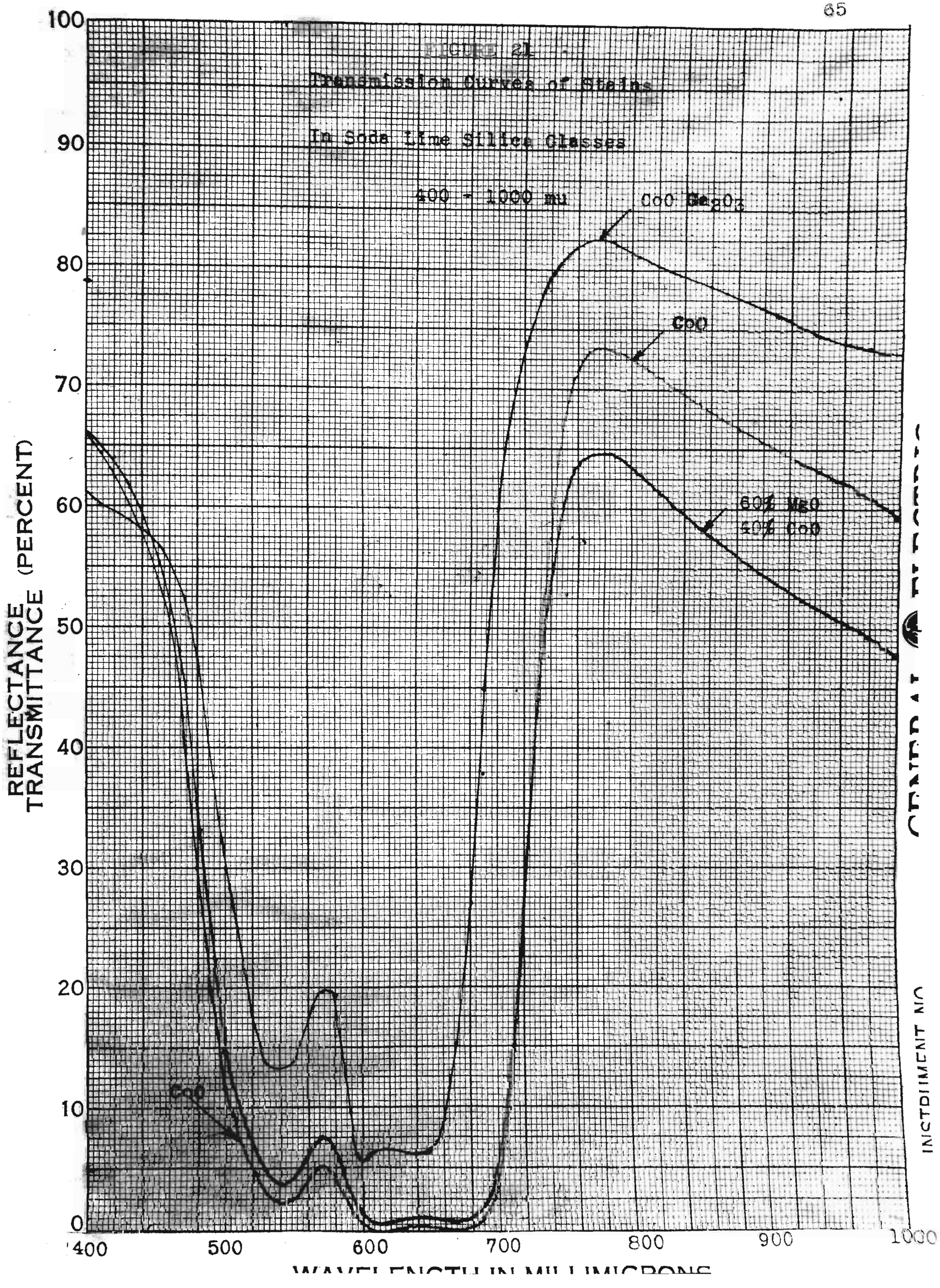

FIGURE 21

Transmission Curves of Stains

In Soda Lime Silica Glasses

400 - 1000 mu

Mill Additions

Frit	100%
Clay	7
Tin Oxide	8
Colorant	.1

The coloring oxide was not placed in the frit due to its fritting temperature, as will be seen later. Upon firing, the stains were fairly well disseminated throughout the enamels; however, there were slight indications of colored streaks indicating that complete solubility had not taken place. The reflectance curves are shown in figures 22 and 23 and the color data is given in table 14.

Finally the stains were placed in a fritted lead glaze of the following composition:

Frit

Feldspar	20.5
Boric Acid	15.5
Flint	22.9
Pb_3O_4	24.2
$CaCo_3$	16.8

Glaze

Frit	65.9%
Feldspar	18.0
Clay	7.28
Flint	5.44
ZnO	3.33
Colorant	.10

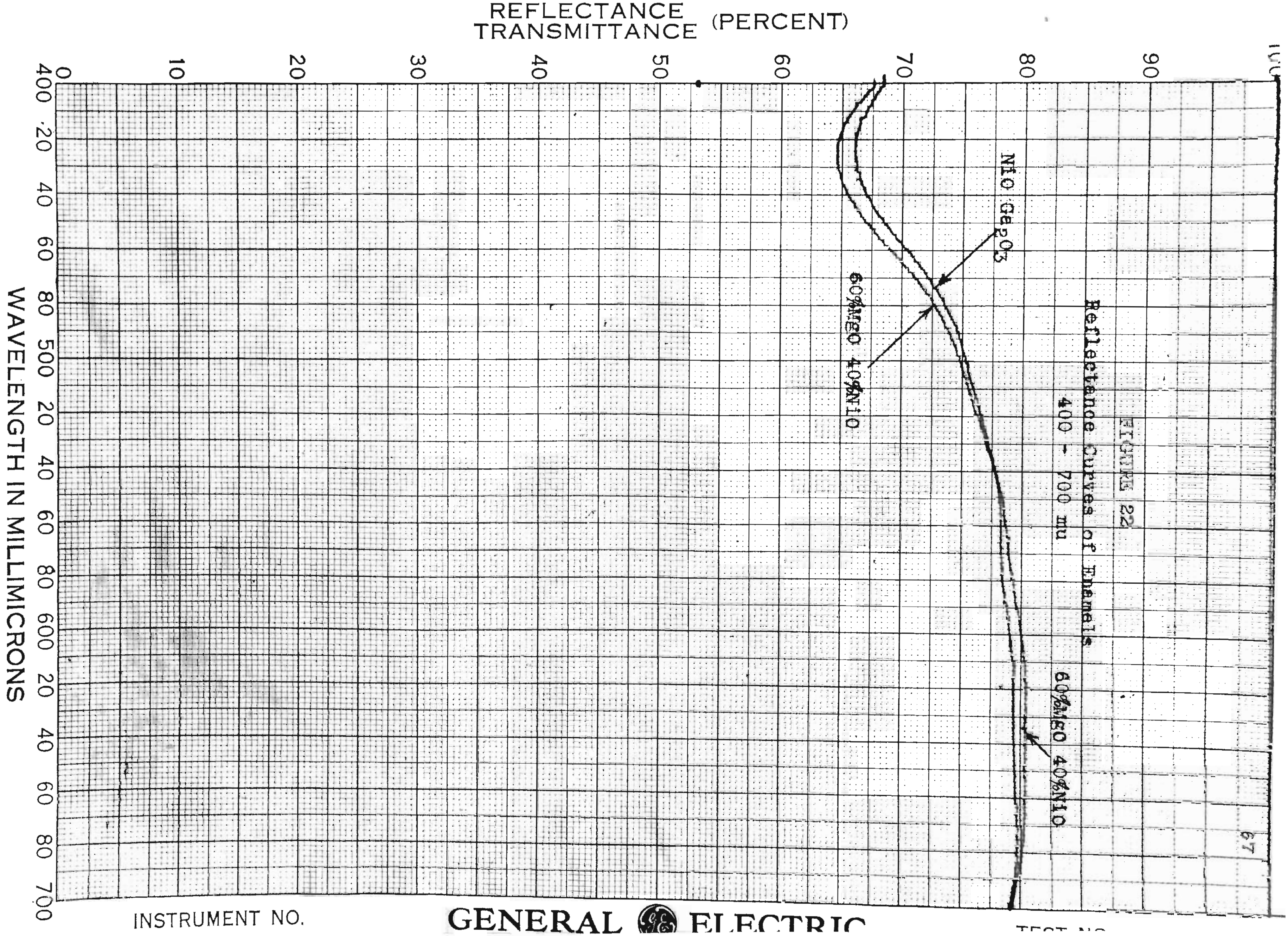

FIGURE 22
Reflectance Curves of Enamels
400 - 700 mu

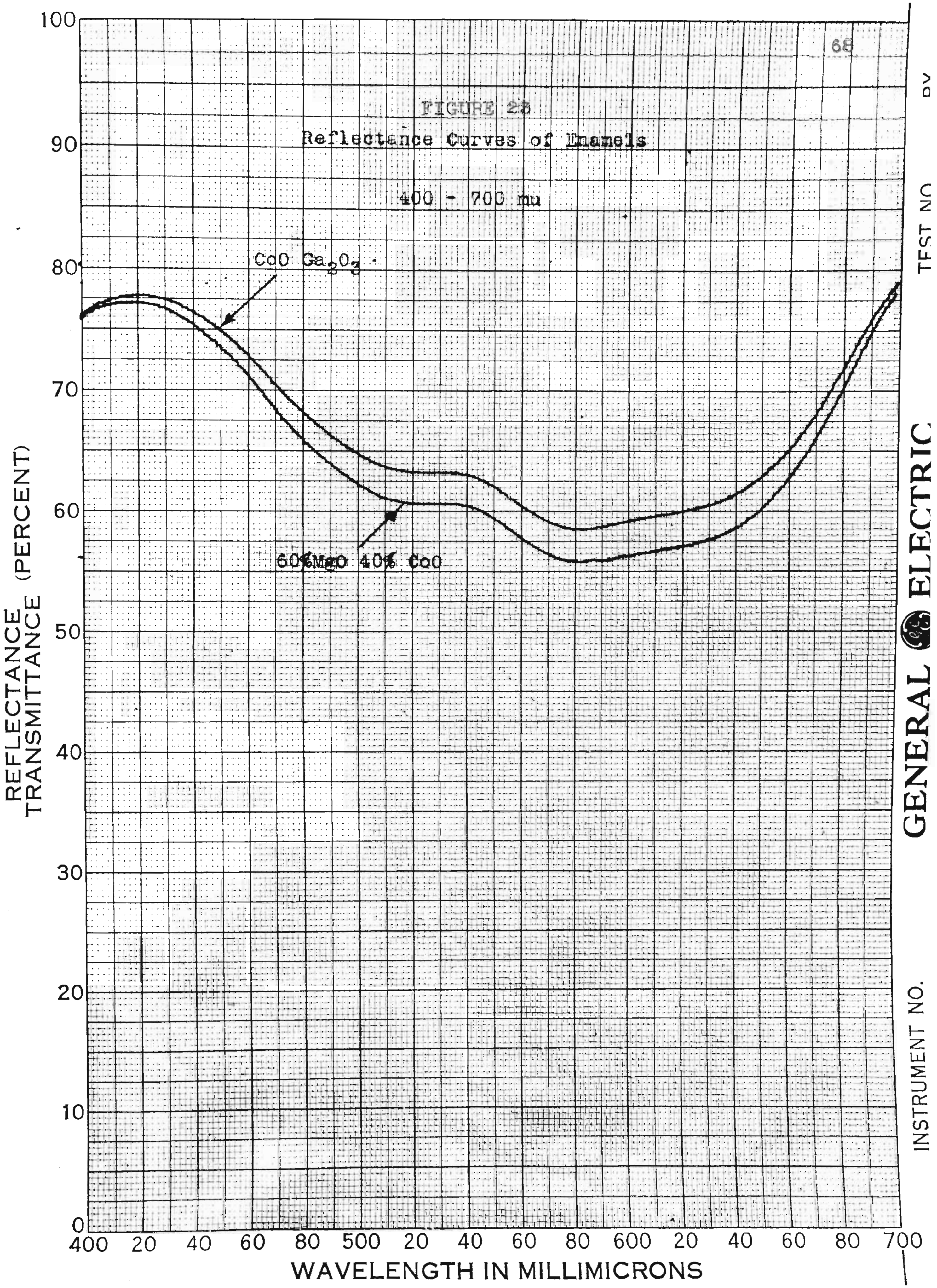

FIGURE 23

Reflectance Curves of Enamels

400 - 700 mu

The firing of these samples showed complete solubility at the maturing temperature of the glaze (Cone 4).

DISCUSSION OF RESULTS:

In the system NiO-CoO, the previously reported solid solution was verified. This system made it evident that for this investigation back reflection would have to be employed for accurate determinations. No color other than the characteristic blacks of the NiO and CoO were noted.

The TiO_2-WO_3 system gave absolutely no indication of promising colors. The forward reflection showed definitely the presence of both the parent materials.

The systems Cr_2O_3-V_2O_3 and Fe_2O_3-V_2O_3 could not be prepared due to the fact that the V_2O_3 could not be obtained at the desired temperatures. No attempt was made to use an inert atmosphere with these systems.

In the systems ZrO_2-NiO and ZrO_2-CoO, no color resulted. The report that ZrO_2 forms a cubic solid solution with concentration of 4 to 40% MgO could not be conclusively verified. The forward reflection x-ray patterns gave definite indications that the parent materials were present as such.

The system MnO-ZrO_2 could not be thoroughly investigated since MnO could not be kept from oxidizing at the desired temperatures. In the casting of the inert gas chamber, it was found that a very slow drying, firing, and cooling schedule must be observed when dealing with solid or thick alumina castings.

In the systems NiO-MgO and CoO-MgO, the solid solutions previously reported were verified; however, neither were found to obey Vegard's rule, which says that for two materials of similar crystal structure and forming a continuous series of solid solutions, the lattice constants are a linear function of the composition. Vegard's original paper was not available as a reference but apparently the term composition has been misunderstood. Channel-Evans and Hume-Rothery say atomic percent composition, while Passerini, although he does not say so, but it can be calculated from his given data, has used weight percent. Naturally this interpretation of the data would lead to conflicting results.

Jette has suggested a very general approach to the question of solid solubility.(41) (Again this reasoning is for metallic alloys; however, there is no apparent reason why it will not apply to oxide systems). He has drawn an interesting analogy between Raoult's law of solutions and Vegard's law of solid solutions.

Raoult's law holds only when the molecular species present are very similar chemically and physically and Vegard's law of additivity holds when the atoms of the materials involved are very nearly the same size and of

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(41) Eric Jette, Intermetallic Solid Solutions, A.I.M.M.E. Trans., Vol. 3, p. 75, (1934)

similar electronic structure.

Negative deviations from Raoult's law result from the operation of specific attractive forces, which, when extreme, lead to compound formation. Jette points out that negative deviations from Vegard's law occur in those alloy systems in which intermetallic compounds are formed.

Positive deviations from Raoult's law are those thought to be due to repulsive forces between unlike molecules or a tendency for like molecules to associate. Positive deviations from Vegard's law are not all clearly understood. Here, also, the deviation is probably due to repulsive electro-static forces or unlike atoms. Jette again has pointed out that all metal pairs whose solid solution is known to show a positive deviation are made up of at least one transition element, and one member of the pair being capable of occurring in at least two valence states.

Dr. R. F. Mehl, in discussion of Jette's article, says that he believes a plot of a_o^3 is more appropriate to plot against atomic percent instead of a_o alone, since the atoms and molecules actually do exist in three dimensions.(42) He also points out an exception where a compound is formed and still there is positive deviation from Vegard's rule.

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(42) R. F. Mehl and B. J. Mair, Chemical Affinity in Metallic Alloys, J. Amer. Chem. Soc., Vol. 50, pp. 55-73, (1928)

Grum and Grzhimails say that Vegard's rule is only approximate,(43) since it does not take into account the modification of the effective volume of an atom by chemical combination. B. Ya. Pines, in his investigation of Vegard's rule,(44) found that deviations show correct sizes and magnitude of deviations in all cases, except those in which transition elements are present. He attributes these anomalies to changes corresponding to the building up of the electron shells.

In this investigation, the values of a_o and a_o^3 were plotted against atomic percent and weight percent. When the weight percent was used a positive deviation was obtained in both cases, but when molecular percent was used a negative deviation was obtained in both cases. The closest approximation to a straight line was obtained when a_o^3 was plotted against molecular percent and these curves are shown in figures 9 and 11.

From the above discussion of Vegard's rule, it might be possible to have a positive deviation, since Ni and Co are both transition elements and are capable of existing in more than one valence state. On the other hand, a negative deviation may exist even though no intermediate

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(43) Grum and Grzhimails, Compt. Rend. Acad. Science U.S.S.R., Vol. 33, pp. 237-40, (1941)

(44) B. Ya Pines, Solid Solution, J. Physics U.S.S.R., Vol. 3, pp. 309-19, (1940)

compounds are evident, since there are exceptions to the rule, as pointed out by Dr. Mehl.

Passerini's x-ray results agreed fairly well as a linear relationship; however, his data does not seem too reliable. He has calculated an a_o for each line and taken an average. For one sample his values vary from 4.08 to 4.19 and his average comes out to be 4.18.

To account for the color when these solid solutions were developed there is apparently some temporary modification of the constraints along the three axes caused by the exchange of the atoms in the lattices which change the vibrational frequencies from those of the characteristic MgO, CoO, and NiO, to those of the green given by the NiO-MgO and the pink by the CoO-MgO solid solution.

From the color data, it is evident that the particle size of the powder makes no difference in the dominant wave length, that is, within the experimental error of sample preparation.

It is also seen that the type curve for each component is almost identical. The dominant wave length of the NiO-MgO system varies only 1.2% and the CoO-MgO system varies only 1.3% throughout the system, indicating that the color of each of the components are practically the same. Of course, the purity and the relative brightness vary with each component.

These stains are not soluble in a B_2O_3 glass, and in a soda-lime-silica glass they are not stable. That is, the green given by the NiO-MgO powder and the pink given by the CoO-MgO powder reverts back to the characteristic solution colors of CoO and NiO in this glass. This is definitely shown by the fact that the same glass batches were mixed with the stains and then with corresponding percents of CoO and NiO, the dominant wave length of these glasses are almost identical, within .2%. These glasses give considerable transmittance in the infra red; however, this does not seem abnormal since the glasses with CoO and NiO alone give similar results. The effect that the MgO has on the glass is not known, except that it probably enters the structure as a modifier.

It is evident from the x-ray data and the calculated densities that the spinels $NiO \cdot Ga_2O_3$ and $CoO \cdot Ga_2O_3$ do exist. No extensive investigation was made to determine applications except the possibilities as colorants in glasses. In B_2O_3 glasses these compounds were not soluble. In a soda-lime-silica glass the stains were not stable. They reverted back to the characteristic solution colors of CoO and NiO, and it is assumed that the Ga_2O_3 entered the structure of the glass as a modifier. Since it is so refractory, it possibly would make the glass more refractory.

The powdered samples gave a considerable reflectance in the infra red and the glasses gave a corresponding transmittance except that the latter curves were the characteristic CoO and NiO type.

In the enamel batches the stains were apparently only partially soluble, since slight streaks could be seen on the surface. However, the color data indicates that the color imparted to the batch, in all cases, reverted to a characteristic solution color. In the glazes the stains were completely soluble, but again, in all cases, they were solution colors.

By using the four types of glasses it was hoped that it could be shown that a temperature range did exist in which the stains were soluble and still exhibit the characteristic colors of the solid solutions and spinels. This is the reason for not employing the colorant in the frit of the glaze and enamel. It is apparent from the data, however, that, as soon as the stains become soluble, they revert back to a solution color.

In the comparison of the color of the aluminate spinels with the gallium spinels it can be seen that the nickel compounds give stains whose dominant wave lengths are in the same order. The cobalt aluminate, however, gives a dominant wave length in the purple region, even though, visually, it looks to be a royal blue. The percent conversion may account for this, since the purity of the aluminate spinels is not known, whereas, back reflection data indicates that the gallium spinels are pure. Nevertheless, the type curves are practically identical, and no apparent anomalies are present. (See

FIGURE 24

Reflectance Curves of Aluminate Spinels

400 - 1000 mu

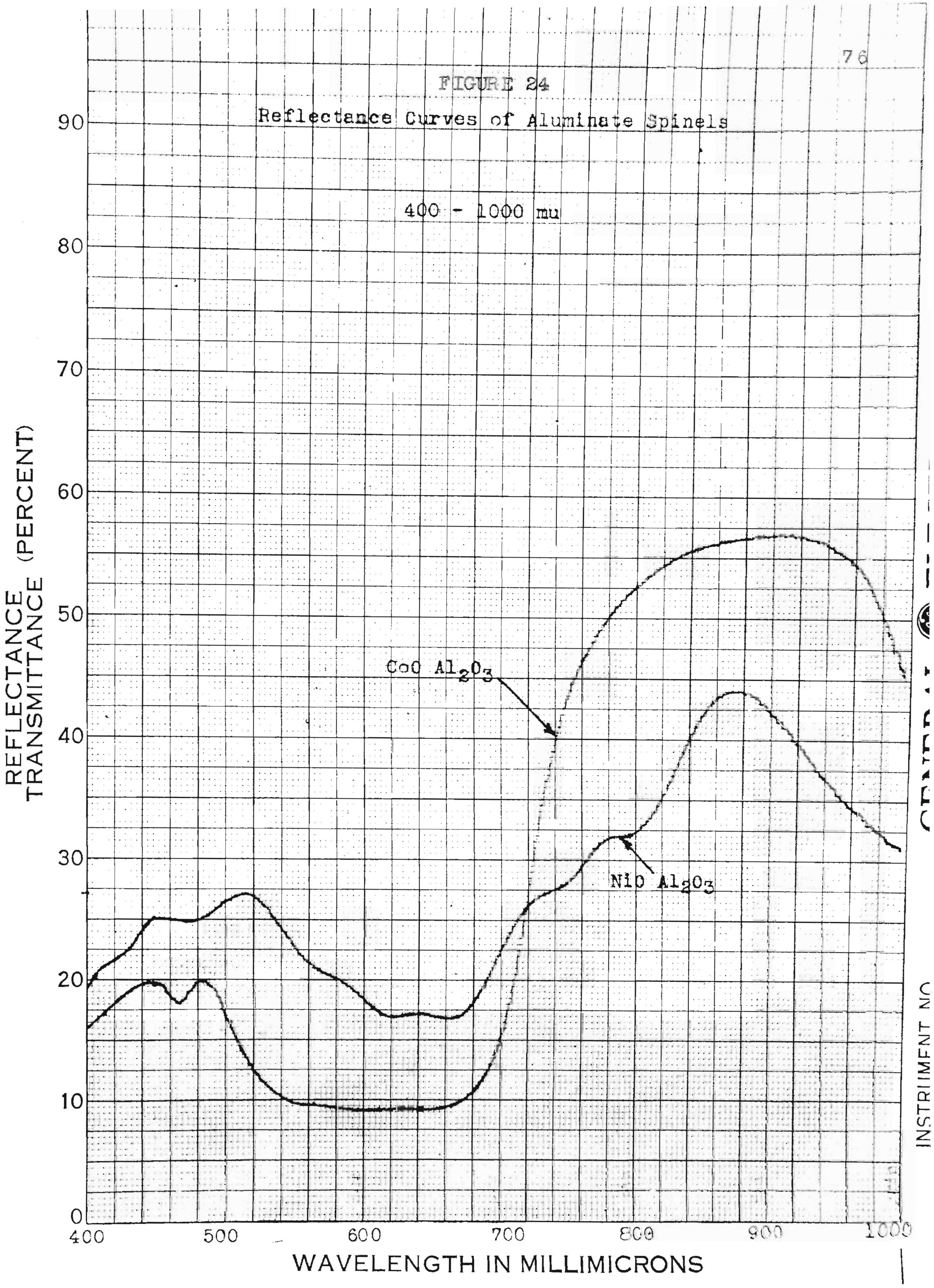

figure 24).

CONCLUSIONS:

From the results of this investigation, the following conclusions may be drawn:

1. No color modification takes place as a result of a solid solution in the following systems:

(a) NiO-CoO

(b) TiO_2-WO_3

(c) NiO-ZrO_2, CoO-ZrO_2

(d) Cr_2O_3-Ga_2O_3, Fe_2O_3-Ga_2O_3

2. A color modification does take place as a result of a solid solution in the following systems:

(a) MgO-NiO

(b) MgO-CoO

3. The resulting stains of the NiO-MgO and CoO-MgO systems are not stable in glass batches. They revert to the characteristic solution colors upon becoming soluble.

4. Particle size below 100 mesh of the stains make no difference in the color of the powdered stains. The finer particle sizes aid in sample preparation.

5. The lattice constants of the NiO-MgO and CoO-MgO system do not follow Vegard's additivity law, instead, a negative deviation is noted.

6. The compounds NiO-Ga_2O_3 and CoO-Ga_2O_3 do exist as spinels.

(a) As stains they are not stable in glass batches when they become soluble, but revert to characteristic solution colors.

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VITA:

Bobby L. Mornin, the son of Mr. and Mrs. J. W. Mornin, was born in Herrin, Illinois, November 20, 1923. He attended the public schools in Herrin, graduating from high school in 1942. He entered the University of Illinois in 1942 and completed one semesters work before being called to the Armed Forces. He received his discharge from the Army in 1946, and entered the Missouri School of Mines, and was graduated in 1948 with the degree of Bachelor of Science in Ceramic Engineering.

He enrolled in the Graduate School of the Missouri School of Mines in September, 1948, the recipient of the Edward Orten, Jr. Ceramic Foundation Fellowship, and was graduated with the degree of Master of Science in Ceramic Engineering in 1949.