Colors Developed by Cobalt Oxides[1,2]

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The colors which cobalt oxides exhibit either as hydrous oxides or in sintered or fused masses with metallic oxides, borates, and silicates are so characteristic as to afford valuable individual tests in qualitative analysis, and so brilliant in some cases as to serve as pigments. Although these facts and applications have been known and applied for a long time (even the ancients having used cobalt blue as a pigment), no effort has been made to classify the color phenomena.

With the scattered data collected, it is the purpose of this paper to offer an hypothesis which will account for the apparently erratic color effects shown by the numerous oxides, alone, hydrated, or in physical or chemical combination with metallic oxides and fluxes.

HISTORY

The data which are here collected have been arranged according to composition and not chronologically. The name and formula of the substance are given, with methods of preparation and properties.

CoO—COBALTOUS OXIDE—Formed by heating Co_3O_4 in nitrogen. When heated in air it oxidizes to the black higher oxide. It is not oxidized at ordinary temperature even on long standing. It is soluble in warm concentrated potassium or sodium hydroxide solution, yielding a deep blue color.

Color: Light Brown:[1]* Formed by ignition of Co_3O_4 in carbon dioxide.[2]
Color: Brown: Formed by reduction of Co_3O_4 with hydrogen.[3]
Density: 5.68;[4] 6.7.[5]

Co(OH)₂—COBALTOUS HYDROXIDE—Formed by the precipitation of cobaltous salts in absence of air with concentrated potassium hydroxide, yielding blue basic salts which go over through violet into a rose-red hydroxide (more rapidly when warmed).[6,7]

Boiling cobaltous carbonate with potassium hydroxide solution forms a voluminous blue oxide, which turns violet and then yields a rose-red hydrate.[8,9]

It can also be formed by heating a solution of 10 g. of $CoCl_2 \cdot 6H_2O$ in 60 cc. of water with 250 g. of potassium hydroxide under an atmosphere of illuminating gas; the cobaltous hydroxide dissolves, yielding a blue color. After 24 hrs. the precipitated crystals are washed with water.[10]

The alkaline solutions contain the cobaltous hydroxide as a colloid since it is not dialyzable and is precipitated on barium sulfate by shaking with the latter. This is true also of the blue alkaline solution in glycerol and also of the green solution obtained by oxidation with air.[11]

Hantzsch[12] found that the blue precipitate obtained at first when cobalt salts were precipitated by alkalies was cobalt salt. In the absence of the latter, i. e., with excess of alkali, the blue changes quickly to the pink hydroxide.

In some experiments carried out at New York University, the authors have shown that the pink hydroxide may be changed to blue by allowing it to stand in contact with cobalt solutions.

MAGNESIUM COBALTITE—When magnesium oxide is heated with cobalt nitrate it takes on a pale rose-red color. Minerals which contain magnesium also take on a rose-red color, upon heating with cobalt nitrate, when aluminium oxide or other heavy metallic oxides are absent.[13] When a mixture of neutral cobalt chloride and magnesium chloride is treated with ammonia a green precipitate forms, which contains nearly 10 per cent of magnesium oxide, remains green upon washing, is insoluble in ammonia and ammonium carbonate, but slightly soluble in ammonium chloride imparting a dirty yellow color, and can be reprecipitated by potassium hydroxide.[13]

$(Mg.Co)O.Al_2O_3$—On fusing 5 parts of Al_2O_3, 2.4 parts MgO, 20 parts CoO and 4.7 parts fused B_2O_3 in a platinum dish and dissolving the flux in hydrochloric acid, regular octohedra remain which will scratch glass. When less cobalt is used blue spinels form.[14,15]

$2MgO.CoO.B_2O_3$—Made by Ebelmen[16] according to Mallard's[17] method. The product is composed of an isomorphous mixture of $3(MgO.CoO)2B_2O_2$, which according to Guertler[18] possesses the formula $2(MgO.CoO)2B_2O_3$, since the formula of the compound $3MgO.2B_2O_3$ in reality is $2MgO.B_2O_3$.

$3CoO.2B_2O_3.4H_2O$—Formed by precipitating cobalt sulfate with borax. Color, reddish white.[19]

$3CoO.B_2O_3$—Made by fusing cobaltous oxide with B_2O_3. Rose-red rhombic crystals form.[16] Formula corrected by Guertler to $2CoO.B_2O_3$.[18]

$CoO.Al_2O_3$—COBALTOALUMINATE—When aluminium oxide is heated with cobalt nitrate or when a mixture of iron-free alum and a cobalt salt is precipitated with an alkali, a bright blue precipitate forms.[20]

THENARD'S BLUE—The composition varies, depending on the method of manufacture. Sometimes it is cobaltous oxide and aluminium oxide; other times it is phosphate or arsenate of cobalt. It is best prepared by first precipitating a solution of a cobalt salt, usually the iron- and nickel-free nitrate, with potassium or sodium phosphate or with sodium arsenate. The gelatinous, violet precipitate is thoroughly washed and well mixed with 3 to 5 volumes of freshly precipitated, well-washed alumina (when cobalt arsenate is used a larger proportion of alumina may be added), precipitated from a solution of iron-free alum by the addition of sodium carbonate. The mixture is dried until it becomes brittle, and heated at a cherry-red heat for 30 min. in a covered clay crucible. When the desired blue color has been developed, the mass is ground with water and dried. In order to prevent the possibility of entrance of reducing gases, which would injure the value of the product Regnault[21] recommended the addition of a little mercuric oxide before the ignition. This decomposes and evolves oxygen, which prevents reduction. The mercury escapes in the form of vapor.

A similar but less fine product is produced by the simultaneous precipitation of the oxide of cobalt and aluminium by the addition of sodium carbonate to a mixture of cobalt nitrate and alum. The mixed precipitate is washed and treated as above.

According to the process recommended by Binder,[22] the oxide of cobalt is precipitated by the addition of the requisite quantity of ammonia to a solution of pure cobalt chloride. The washed precipitate is mixed with alumina as before, dried, and heated at red heat in a clay crucible for 2 hrs.

Thenard's blue is of a fine ultramarine color. The presence of an excess of cobalt imparts a somewhat greenish tinge. It is one of the most permanent blue pigments, being unaltered by acids and alkalies, and is largely used as an oil and water color, though it works better in water alone. It is nonpoisonous, and has the advantage of miscibility with other pigments without alteration.

RINMANN'S GREEN—The first contributions concerning Rinmann's green were made in the year 1780, when S. Rinmann described one of his newly discovered green pigments, which he recommended as a paint color because of its resistance to atmospheric conditions. It appeared that Rinmann was searching for this green pigment, for in one place he writes that he considered it possible to fix the greenish blue color of certain cobalt solutions. He had in this connection tried zinc oxide as a fixing agent, for he precipitated a cobalt and zinc solution with

calcium carbonate, dried the precipitate and ignited it, and found that the green color obtained corresponded in minutest detail to the color of the above-mentioned cobalt solution. He observed that the mass became green at low red heat, but upon being more strongly ignited and subsequently cooled it again turned gray and finally black.

As a possible explanation of the blue-green color, Rinmann assumed the existence of a colored modification of cobalt oxide, the green substance being an additive compound of this blue compound with a yellow metallic oxide. However this explanation did not hold when other oxides were examined. It is, however, of interest to note in connection with the explanation which is to follow, that Rinmann had suspected this substance to be of a mixed color.

From the end of the eighteenth century to the middle of the nineteenth, however, one searches in vain for information concerning Rinmann's green. The industrial investigations concerning this substance have been carried out technically rather than chemically. At best, one finds only very indefinite suppositions concerning the reactions involved.

Researches by Hedvall[23] with a view to preparing Rinmann's green in crystalline form, resulted in the formation of cobaltous oxide crystals in octahedral and prismatic form, similar to those obtained by Lachaud and Lepierre. Hedvall found that he could obtain well-defined cobaltous oxide crystals by heating ordinary cobaltous oxide or cobaltous carbonate several times to 1000° or higher, with, say, four times its weight of potassium chloride. By this method, there are obtained exceedingly beautiful crystals of cobaltous oxide enclosed in the Rinmann's green. They have a dark red color, and the majority of them seem to be octahedra, tetradehra, and a combination of positive and negative tetrahedra. Very often the cobaltous oxide crystals enclosed in the crystals of Rinmann's green are surrounded by a brighter green region than Rinmann's green. Often they are embedded in the cobaltous oxide.

Hedvall has accepted an hypothesis of L. Storch[24] to explain the color of Rinmann's green. According to Storch, there exists a blue modification of the lower oxide of cobalt which gives a green color with the yellow zinc oxide. This blue modification is not stable unless zinc oxide is present. It is thought that Rinmann conceived of it as early as 1780. One meets it again in the work of J. Bersch. Doubtless the opinion is a relic of the time when chemists established the properties of the metallic oxides from those of the salt. In any event, it is not very probable because: (1) This blue modification has never been prepared; (2) zinc oxide is yellow when hot; crystalline zinc oxide is exceedingly pale yellow with a tinge of green. This color change rests upon the fact that the absorption spectrum of the zinc oxide moves with the rise of temperature from the ultraviolet to the visible part of the spectrum and not upon the formation of a new modification. Such shifting of the absorption spectrum with the temperature is quite general.

In nature, crystalline zinc oxide occurs as the rare mineral zincite, which crystallizes in hexagonal semimorphous prisms and pyramids. Gorgeu[25] states that by heating zinc sulfate with an alkali sulfate there are formed greenish yellow, hexagonal prisms and tablets with high refractive index.

The question which deserves consideration is: Is Rinmann's green a compound, and in what way is one to conceive of its structure? The substance was made by Hedvall from a mixture of zinc and cobalt carbonate or oxalate, or the oxide mixture which results from the heating of the salts. This mass was again heated with or without a flux of potassium chloride to 1100° and 1300° to 1400°. A platinum crucible was used in every case since it was shown that the cobaltous oxide united with the silicate glaze of porcelain crucibles.

When Rinmann's green is prepared according to this method the contents of the crucible become greenish yellow even at red heat. The mass is not molten and does not appear homogeneous. Upon cooling, the surface becomes grayish black, the inner part retaining its yellowish green color. At white heat, the color becomes almost green when proper proportions of the oxide have been used, and the color is not changed when cooled in an atmosphere of carbon dioxide; when cooled in air, however, the surface becomes black, as a result of the formation of Co_3O_4.

In all these experiments Hedvall found that in a blast furnace at 1100° or in a porcelain furnace from 1300° to 1400° Rinmann's green and its two components, cobaltous oxide and zinc oxide, were always obtained in crystalline form. When no fusion mixture was used, large crystals or a homogeneous mass did not result. The product was composed of exceedingly small crystals of Rinmann's green and one or both of the components. That they were crystalline could be observed when magnified in polarized light. From this experiment, it was thus possible to prepare Rinmann's green in crystalline form.

An attempt was made to separate the components of the melt, namely, cobaltous oxide and Rinmann's green. This was not possible with chemical reagents, as all the solvents tried, such as hydrochloric, sulfuric, nitric, and acetic acids, potassium hydroxide, ammonium hydroxide, ammonium carbonate, and potassium cyanide, reacted upon the cobaltous oxide as well as upon the Rinmann's green. A preliminary determination showed that the specific gravities of these two substances are too high and too near each other to accomplish a separation in this way. To get larger crystals of Rinmann's green, the usual methods were pursued, *i. e.,* the addition of a fusion mixture and slow cooling.

In this connection many substances were examined. With calcium chloride and B_2O_3 it has been proved that a cobalt borate is formed, and upon boiling the flux with potassium carbonate a characteristic green solution is formed, probably of the same kind as that obtained by the decomposition of cobaltous hydroxide. The percentage figures of flux are so computed that the original mixture of zinc oxide and $CoC_2O_4 \cdot 2H_2O$ corresponds to 100 per cent. When a mass is quoted as being CoO–0.3, ZnO, 100 per cent ICl, it denotes the presence of one molecule of CoO to three molecules of ZnO; for example, 1 g. CoO (1/75 mole = 2.49 g. oxalate or 1.55 g. carbonate) corresponds to 3.25 g. ZnO (3/75 moles) and 5.7 g. KCl. In order to investigate under what conditions the largest and best shaped crystals are formed a series of experiments were carried out, partly with different mixtures of flux and partly with varying amounts of the two oxides. Hedvall found that a mass of the composition 1 CoO.1 ZnO with 60 to 70 per cent KCl was not yet molten at 1100° C., and only a few crystals of Rinmann's green and cobaltous oxide had formed. Often these fused together, and well-defined crystals formed from the inside of the crucible in a remarkable fashion, from 0.5 to 1 cm. large. They collapsed, however, as soon as they were boiled with water. This same mass was then heated at the same temperature with 100 per cent potassium chloride for 3.5 hrs. and cooled in carbon dioxide. After removing the flux a dark green substance remained, composed of red and green crystals. Some of the green crystals were large and well defined and made up of hexagonal plates or pyramids of a beautiful green color. Frequently a zone structure could be observed. The red crystals often appeared enclosed in the green and were well-formed octahedra or tetrahedra. With this last proportion of flux and oxides and at this temperature, therefore, a well-crystallized Rinmann's green can be formed.

Since the yield of large crystals was very small with only one ignition, the operation was repeated several times. Each time new mixtures of flux were added during ignition, and between each heating the mass was boiled out in order to accomplish thorough mixing, without crushing the larger crystals already formed. Each ignition lasted from 1 to 2 hrs., and after repeated ignitions the yield was increased, as well as the formation and size of the green crystals.

The little red crystals were washed but little at first. The different size of the green and red crystals made it seem possible to separate them with a sieve whose mesh was large enough to let the small crystals through and to retain the large ones. A completely homogeneous Rinmann's green could not be obtained in this way, however, for many of the red crystals are enclosed, as mentioned before, and these, of course, could not be removed. A uniform red substance was naturally impossible to get in this case. However it was possible to make a few tests.

The green crystals were washed in the usual manner preparatory to the analysis. A weighed amount of substance was dissolved in hydrochloric acid, the solution heated, and the escaping gases were dissolved in potassium iodide solution. By this treatment no iodine came off; therefore no peroxide could be present. Rinmann's green, therefore, contained only divalent cobalt.

Analysis of Red Crystals—It is natural to suspect that the red crystals are composed of cobaltous oxide. The strongly heated cobaltous oxide, as mentioned before, is very insoluble in acids. The crystals of Rinmann's green are easily soluble even in weak acids. A small amount of the above-mentioned mixture, after passing through the sieve, was treated for 12 hrs. with acetic acid and filtered from insoluble substance. The insoluble substance appeared entirely homogeneous under the microscope and consisted of crystals which looked like cobaltous oxide crystals. This substance was not completely soluble in concentrated hydrochloric acid. Only upon treatment with concentrated sulfuric acid did it go entirely into solution.

Even upon treating the residue with acetic acid, no zinc could be detected. An analysis was carried out on a weighed amount of this residue, 0.1631 g. (insoluble in acetic acid) gave 0.1272 g. of Co = 78.47 per cent cobalt, computed as CoO = 78.67 per cent. Cobalt as a metal was identified after reduction in a stream of hydrogen.

In order to ascertain where the boundary lay for complete reaction between the zinc oxide and the cobaltous oxide a series of masses (1.7 moles ZnO to 1 mole CoO with 100 per cent potassium chloride) were heated in a porcelain furnace in sealed tubes.

Von Delasse has given a method for determining the percentage composition of stone containing more than one mineral. Later his method was simplified by A. Rosival. The number of scale parts was calculated which was due to each constituent in a preparation. This number (a uniform division of the constituents was assumed) was set in proportion to the volume of substance concerned. When the specific gravity of the total material and of each constituent was known, it was easy to go from the per cent volume to the per cent weight. Thus a large number of scale divisions were calculated. Taking the Constituents A and B, for example, and considering each scale division as a and b:

$$\text{Per cent volume A} = \frac{100a}{a+b}$$

$$\text{Per cent volume B} = \frac{100b}{a+b}$$

If now the specific gravity of the total substance (A + B) = S, from which A = S_A and B = S_B we have:

$$\text{Per cent weight A} = \frac{100a.S_A}{(a+b)S}$$

$$\text{Per cent weight B} = \frac{100b.S_B}{(a+b)S}$$

If $(a + b)$ is a larger number and the preparation is as homogeneous as possible, the accuracy of this method is then sufficient to warrant combining the results of this calculation with those of chemical analysis.

To carry out this impurity calculation, microscopic preparations were made, two for each fusion. These were so prepared that the melt could be ground or the purified mass of flux be divided on the object glass, in powdered form. When the cover glass was put on the object glass, part of the preparation spurted off toward the edge. This portion was gathered and put on a second slide so that the calculations gave the same proportions as in the preparation at hand. Much effort was required to get a uniform diversion, and the mixture index was very great in each case (4–10,000 scale divisions). The fusion was always removed from the slides which were prepared for an analysis. All the calculations were carried out with a Zeiss microscope with a 760 enlargement.

From several of these determinations Hedvall concluded that Rinmann's green had no definite composition. If, then, Rinmann's green is not a chemical compound, it may be a case of solid solution. If one accepts zinc oxide as a solvent, it then follows that we are dealing with a dilute solution.

Action of Flux—From what has preceded it is clear that the fusion mixture is of the greatest importance to the growth and formation of the crystals. In some of the fusions, the fusion mixture was increased 100 per cent. The same proportions of zinc oxide and cobaltous oxide were used as in the former cases. From a mass of 0.1 CoO, 0.1 ZnO with 100 per cent potassium chloride, only small, poorly shaped crystals were obtained. With 100 to 200 per cent potassium chloride, large hexagonal prisms and tablets were formed. This relation held only for the above-mentioned fusions. With increasing amounts of zinc oxide the formation of needle-shaped crystals became proportionately difficult. Often the crystals separated from the melt as skeletons. It is evident that these different crystalline forms are dependent on the different viscosities of the fusion mixture. It is also evident that the reaction between the two components, cobaltous oxide and zinc oxide, is entirely or nearly complete, in the presence of fusion mixtures so that only one compound occurs with the Rinmann's green, while in the mass without fusion mixture Rinmann's green and both components are present.

To prove this, Hedvall divided a mixture of 1 CoO : 3 ZnO into two equal parts. To Sample 1, 100 per cent potassium chloride was added; to Sample 2, no flux was added. Both were heated three times at 1100° under the same conditions. Between each ignition the substances were well mixed and a new portion of potassium chloride was added to Sample 1 to replace that which had volatilized. After Sample 1 was freed from flux slides were made of each. Calculations were made in the usual way.

Two methods were used to obtain analyzable material. One was based on the fact that Rinmann's green crystals grow on successive heatings, while cobaltous oxide crystals do not. To get a product as pure as possible by this method, a mass was used which would contain cobaltous oxide in excess inasmuch as zinc oxide would be much more difficult to separate. In this way, the yield became very small. After some fifteen or twenty heatings, about 3 per cent of the calculated mixture was retained and this process took about a week. The crystals were prepared for analysis, while the flux was being removed with water. The crystals were then washed on the sieve with anhydrous benzene in order to remove the cobaltous oxide crystals as much as possible. The substance was then pulverized, thoroughly mixed in an agate mortar, and analyzed. At the same time an impurity calculation of the substance analyzed was carried out on a microscope slide.

The other method corresponded with the one of heating in a porcelain furnace. Most of the fusions which were made resulted in products which were of such a high degree of purity as to warrant analysis by the microscopic method. The slides were prepared from the mass used for analysis. The values obtained were not the same as those which were prepared from the fusion. It is reasonable of course to expect that the substance after much washing did not have the same composition as it had before.

Determination of Specific Gravities—As was previously stated it was necessary to know the specific gravity of these different substances in order to be able to calculate the amount of im-

purity. These determinations were carried out in benzene (sp. gr. 1.8847 at 17.5° C.). Determinations were made with crystals of cobaltous oxide and zinc oxide formed at 1100° and 1300° to 1400°, respectively.

In some cases the specific gravity of Rinmann's green was between those of the constituents. In other cases it was lower than that of the constituents. The deviation, however, was small. Aside from these, differences between the specific gravity of the flux and that of the components below it were so small that the calculated impurity could be used with safety. In most fusions the impurity was so small that it was negligible in the analysis error. Summarizing these facts, Hedvall concluded that the different fusions gave Rinmann's green of varying composition. From this it is clear that these substances can be no chemical compounds but rather a solid solution between the two components, cobaltous oxide and zinc oxide. These two substances form with each other a series of mixed di-isomorphous crystals; while zinc oxide crystallizes hexagonally, cobaltous oxide in general, at least, crystallizes regularly. Only in a few cases where the larger crystals of Rinmann's green were obtained was it possible to determine crystal structure and in those cases it was hexagonal. Whether or not it gave a regular form (with large mixtures of cobaltous oxide) was not proved; at least, not in the fusion of 1 CoO and 1 ZnO. At any rate, according to Weber, a regular crystalline form of zinc oxide is known.

It can be concluded from the investigation that the formation of Rinmann's green takes place at red heat, but much more quickly at higher temperatures. It is not necessary, however, that the mass liquefy, for the masses which do not contain flux give a Rinmann's green of the same appearance; but in this case the conversion between the cobaltous oxide and the zinc oxide is not complete. We have here, then, in all probability an example of diffusion in solid substances.

$CoO.V_2O_5$—COBALTOVANADATE—Normal vanadate yields a reddish yellow precipitate with cobalt salts. Acid cobalt vanadate is water-soluble and when treated with acid in aqueous solution a reddish yellow precipitate forms. (Berzelius.[18])

When cobalt nitrate is treated with ammonium metavanadate in a completely neutral solution it yields an orange-yellow precipitate. When heated it has the composition $CoO.V_2O_5$. Cobaltovanadate can also be formed by the conversion of potassium vanadate with cobalt salts.

$CoO.V_2O_5.H_2O$[26,27]—This substance may be prepared by displacing ammonium vanadate with an excess of cobalt nitrate in acid solution with nitric acid, and warming. Garnet-red, rhombic prisms form which are soluble in water.[28] When heated, the color becomes darker with loss of water. According to Radau[27] it is not probable that normal vanadate forms under the conditions just mentioned.

$CoO.2V_2O_5$—An ammoniacal solution of cobalt salt gives with NH_4VO_3 a greenish precipitate, which on exposure to air takes up oxygen. At 100° it becomes reddish brown and upon heating a black product is formed of the above composition(?).[26]

$K_2O.2CoO.5V_2O_5$ (16 OR 16.5 H_2O)—POTASSIUM COBALTO-VANADATE—This substance forms when a 20 per cent solution of KVO_3 is mixed at room temperature with 100 cc. of cobalt sulfate solution containing 18 g. of the salt. A reddish yellow crystalline precipitate forms which is slightly soluble in water and completely soluble in acids. It can also be prepared by mixing a solution of 20 g. KVO_3 in 200 cc. water with a solution of 20 g. cobalt sulfate in 200 cc. water; after warming on the water bath, 70 cc. of 25 per cent acetic acid are added, whereby the yellowish red precipitate which first forms redissolves. The dark red solution yields glistening, brownish red crystals.

Another method of preparation consists of mixing a solution of 16 g. of $3K_2O.V_2O_5.10H_2O$ in 400 cc. water with a solution of 11 g. of cobalt sulfate in 150 cc. boiling water, stirring and digesting for some time. The dark red solution yields garnet-

red crystals, which lose one-fourth of their water at 120° and the remainder at 220°. This product is also formed when 12 g. of potassium divanadate are dissolved in 250 cc. boiling water and mixed with 8.5 g. cobalt sulfate in 100 cc. of water. Dark red crystals, having properties similar to those just mentioned, form. 4.8 parts of the substance dissolve in 100 parts of water at 17.5°. [29,27]

$K_2O.3CoO.7V_2O_5.21H_2O$—Prepared by mixing a solution of 20 g. of KVO_3 in 400 cc. of water with 18 g. of cobalt sulfate in 250 cc. of water. At first no precipitate forms, but the solution becomes turbid on standing. Upon evaporation, brown crystalline crusts form, along with little yellowish brown crystalline needles which can be separated from each other mechanically. The latter crystals are the ones sought for.[27]

$6CoO.P_2O_5$—Prepared by heating Braun's so-called luteocobalti metaphosphate, which becomes rose-red upon the addition of concentrated sulfuric acid and red when treated with sodium hydroxide; after removing the sodium hydroxide, the residue for the most part soluble in hydrochloric acid. The undissolved part is a beautiful red and is the product sought for.[30]

$3CoO.2P_2O_5$—COBALTOPYROMETAPHOSPHATE—Remains as a violet powder when $[Co(NH_3)_6].(PO_4H)_3.4H_2O$ is heated. Contains 43.58 per cent CoO.[30]

$7CoO.As_2O_3$—COBALTOARSENITE—When $Na_2O.As_2O_3$ is treated with an excess of cobalt nitrate the following reaction takes place: $7Co(NO_3)_2 + 2(Na_2O.As_2O_3) + H_2O = Co_7As_2O_{10} + 12NaNO_3 + 2HNO_3 + As_2O_3$.

When freshly precipitated, a slimy, very voluminous amethyst-colored mass forms, which upon drying in the air contains 20 per cent of water, losing it at 150°. It is soluble in sodium hydroxide and ammonia, and very soluble in dilute, and sparingly soluble in concentrated, sulfuric acid. When suspended in water and shaken, or better, warmed with barium peroxide it becomes leather-yellow, then brown, and finally black (formation of Co_2O_3). This substance is also very soluble in potassium cyanide, from which it can again be precipitated by acids; barium peroxide does not decompose it in the presence of potassium cyanide.[31,32]

$3CoO.As_2O_3.4H_2O$; OR $Co_3(AsO_3)_2.4H_2O$—COBALTORTHOARSENITE—This substance forms when a 50 per cent alcoholic solution of cobalt chloride is treated with a solution of potassium arsenite made neutral with acetic acid. A bright red precipitate forms which is sparingly soluble in water, but readily soluble in acids. It turns black upon heating.[33]

$2CoO.As_2O_3$ OR $Co_2As_2O_5$—COBALTOPYROARSENITE—According to Proust,[7] this substance seldom forms in the interior of erythrite. It is prepared by mixing dissolved cobalt salt with potassium arsenite containing cobalt arsenite. A rose-red precipitate forms which becomes dark and horny on drying. That which is precipitated by $2K_2O.As_2O_3$ is also $2CoO.As_2O_3$.[34]

From cobalt nitrate and $Na_2As_2O_4$ a violet-blue precipitate forms, which loses arsenious oxide upon heating and leaves a dark blue residue.[35] It forms when cobalt chloride solution is treated with potassium pyroarsenite, $K_4As_2O_5.6H_2O$, as described by Girard.[34,33] If heated in glass vessels arsenious oxide is evolved and colors the glass blue; when treated with a hot solution of potassium hydroxide, it decomposes into cobaltous hydroxide and a blue solution, from which water precipitates the cobaltous hydroxide. It is soluble in nitric acid with evolution of nitrosylsulfuric acid, soluble in hydrochloric acid, and in ammonia, with a dark red color. It is soluble in potassium hydroxide and sodium hydroxide, only when in the nascent state.

It can also be prepared by adding potassium stannite with large excess of potassium hydroxide to a cobalt solution.[36,37]

$3CoO.2As_2O_3.4H_2O$—This substance forms with evolution of much ammonia when potassium arsenite is rapidly added to a solution of cobalt chloride which has been mixed with an excess of ammonium chloride.[34] It can also be prepared by treating a

cobalt salt solution with $K_2O.2As_2O_3$.[35] The fresh precipitate, pale rose-red, gradually becomes heavier and darker, first loses water upon heating with darkening of color, and then arsenious oxide, leaving a beautiful blue flux; upon cooling a solid crystalline residue remains. Potassium hydroxide decomposes the precipitate when heated, with separation of blue cobaltous hydroxide; hydrochloric acid decomposes it and converts it into an arsenate. At 100° it loses 10.3 per cent H_2O ($4H_2O$ = 10.39 per cent).[34] When treated with ammonia a brownish red solution results, and when treated with potassium cyanide a yellowish red solution is produced.[35] Stavenhagen[33] could not obtain $Co_3As_4O_9.4H_2O$ by rapid addition of $K_4As_2O_7.2H_2O$ to a solution of cobalt chloride.

BASIC $4CoO.As_2O_5$ (WATER-FREE)—COBALTOARSENATE—Forms when a solution of cobaltoarsenate, acid with nitric acid, is treated with sodium carbonate. When fused in a porcelain oven cobaltoarsenate crystallizes completely into beautiful prisms. They are deep dark blue; rose-red when powdered, and readily soluble in acids.[38]

The commercial cobaltoarsenate is formed as *chaux metallique* by precipitation of a solution of cobalt nitrate with potassium carbonate, from which $FeAsO_4$ has previously been removed by precipitation. It can also be prepared by the repeated fusion of glossy cobalt with iron-free potassium arsenocobalt, which is then roasted until it is all changed into a red powder.

$$OAs \underset{\displaystyle O—COOH}{\overset{\displaystyle O}{\underset{}{—O}}} Co$$
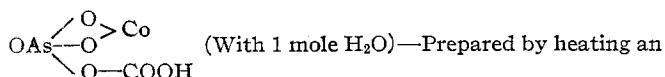
(With 1 mole H_2O)—Prepared by heating an excess of cobalt nitrate solution with sodium arsenate in a sealed tube at 180°. Orthorhombic, blue and reddish violet crystals form.[39,40]

$Co_3(AsO_4)_2.8H_2O$, NORMAL—Occurs in native state as erythrite. The erythrite forms small tuft-like groups of long monoclinic needles, semitransparent, crimson or peach blood-red, and very uniform. Upon drying it is a deep lavendar-blue in color.[41]

It forms as a peach blood-red substance which dries to a dark horny mass when a cobalt salt is precipitated with sodium arsenate.[42]

$Co_3(AsO_4)_2.8H_2O$, ACID—When evaporated in vacuum over sulfuric acid, solutions of cobaltous hydroxide or the normal cobaltoarsenate in excess arsenic acid yield peach blood-red, star-shaped needles, uniting in clusters similar to erythrite, but soluble in water.[43]

$5CoO.2As_2O_5.3H_2O$—When cobaltous carbonate is digested with an excess of arsenic acid solution and the liquid heated in a sealed tube at 235°, pale rose needles form, insoluble in water, and losing their water at high temperatures.[39]

$2CoO.As_2O_5$, WATER-FREE—Prepared from potassium metarsenate and a little cobaltous oxide from which violet knobbed crystals form.[44] When more cobaltous oxide is used, potassium cobaltorthoarsenate yields $2CoO.K_2O.As_2O_5$; upon the addition of cobalt chloride, somewhat opaque, blue crystals form. With sodium instead of potassium, violet, leaf-shaped crystals of $4CoO.2Na_2O.3As_2O_5$ form. Upon the addition of sodium chloride to the orthoarsenate, $CoO.2Na_2O.As_2O_5$, blue transparent prisms form, isomorphous with the manganese and cadmium salts.

COBALT ANTIMONITE—A pale violet, noncrystalline powder is obtained which turns dark green on heating, with loss of water; on strong heating it glistens and possesses a white color and is sparingly soluble in water.[18]

$CoO.Cr_2O_3$—COBALTOCHROMITE—This substance is prepared from a hot solution of cobalt chloride and chrome alum (equivalent quantities) with sodium carbonate, and the bluish gray precipitate is heated. Beautiful dark green crystals form which lack metallic luster and magnetism.[20]

$CoO.2MoO_3.2H_2O$—ACID COBALTOMOLYBDATE—Forms at 100° from $2CoO.4MoO_3$. When heated with a blast lamp it loses water and MoO_3 and changes to the normal violet salt.[45]

$2CoO.4MoO_3.13H_2O$—Forms in considerable quantities as microscopic brown needles, very sparingly soluble in water, after separation of $CoMo_4.H_2O$ from equivalent solutions of $Na_2O.2MoO_3$ and $CoCl_2.6H_2O$.[45]

$CoO.3MoO_3.10H_2O$—Forms when cobaltous carbonate is boiled with an excess of MoO_3 and the solution allowed to evaporate spontaneously. Cauliflower-like knobs of a rose-red color form, sparingly soluble in cold, very soluble in hot water.[46]

$3CoO.7WO_3.25H_2O$—SO-CALLED PARATUNGSTATE—Formed by the addition of boiling sodium paratungstate solution to a cobalt sulfate solution (not the reverse, which results in the formation of double salts). From a fine-grained precipitate it changes to an oily viscous dough-like, rose-red mass of silky luster. The latter solidifies on cooling to a firm powdery mass of the same composition as the fine-grained product, and is bright rose in color, microcrystalline, infusible at red heat, and takes on a bluish color on cooling.[47]

CONCLUSION

On examination of the descriptions of the compounds of cobalt, it is at once obvious that for the most part, they fall into two classes with respect to color: red and blue. The red salts are generally hydrated, and the red hydroxide is the one stable in presence of alkali. The blue salts are generally anhydrous, and the blue hydroxide is stable in the absence of alkali, or in the presence of cobalt salt or cobalt ion.

The writer is doubtful of the correctness of designating many of the combinations as "compounds." In many cases, where these are amorphous they are probably adsorption coagula, and where they are crystalline they are probably mixed crystals whose composition is simple, fortuitously, or because equivalent ratios of constituents were used in their preparation. The very complete research on Rinmann's green illustrates the case of mixed crystals.

Without any intention of exaggerating the analogy, a certain similarity may be noted between tautomeric forms of organic indicators and the two forms of cobalt hydroxide. For example, there is the colorless phenolphthalein, its colorless esters and polysodium salts, and the colored phenolphthalein esters, monosodium salt, and insoluble silver salt. This indicates the inadequacy of any assumptions as to ionization or hydration as an explanation of the color or lack of color of these compounds, and throws the explanation back to the structure theory. Since all phenolphthalein compounds are colorless or red in the absence of other chromophores, so all cobalt oxide compounds, solid solutions, or mere agglomerates are either blue or red, provided no other chromophores are present.

Application of the methods of the recent work done on X-rays and crystal structure will furnish conclusive evidence as to the correctness of this theory. Until such data are available the classification just given must suffice.

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SOCIAL INDUSTRIAL RELATIONS

A Method for Social Research

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In ancient days thunder and lightning were believed to be the work of Jove or Thor. Plagues were thought to be the hand of God laid upon mankind in punishment. Bountiful crops or famine years were similarly regarded as expressions of Divine good will or wrath. Whatever was not understood was believed to be superhuman and impossible of control by man. Individuals and nations submitted to these manifestations of natural force, without question, until men of theoretical science disclosed the laws of electricity, contagious disease, and plant growth; and chemists or engineers followed who applied the theoretical science to the day's work.

The result, nearly all attained within the past fifty years, was evolution of the huge engineering industries which to-day are so commonplace that even the two seemingly superhuman ones, wireless telegraphy and aviation, are in daily commercial use. Each has been reduced to an exact science, which varies in its results only as man is unable to hold the helm true to an unswerving course in an open sea.

THUS THE PHYSICAL FORCES THAT USED TO TERRIFY AND DESTROY have been transformed into power that drives the world's industry.

During this half century of tremendous material transformation, by science applied through research, the forces that direct government, banking, commerce, secondary education and most other mental or spiritual activities, outside applied science, continued to guide these functions in accordance with the ancient belief that individual or national action is subject to few, if any, fixed laws discoverable by man. The leaders of government and commerce saw no analogy between the modern industrial world and the perfect social organizations of the ants or the bees, in which complete specialization of the individual is made completely effective by coöperation. They failed to discern that the new, intricate problems of human relations that arise from complex, industrial, city life can also be solved by science and research as chemical problems are. As they did not grasp this fact, these leaders continued to apply, with few changes, the methods of government and social control that had prevailed since the days of Rome and of England before Watt and Arkwright.

They regarded government, commerce, and social industrial relations as things outside the scope of improvement by experiment and scientific research. They believed each human mind to be a free and independent unit, subject to no general or mass mind law.

WITHIN THE LAST TWO DECADES scientists have appeared who have proved the close similarity of material and mental forces. They have shown that one primary mechanical law and several laws of biology govern the action of the entire modern industrial world. One of these practical scientists, Roger W. Babson, a Massachusetts Institute of Technology engineer, has applied the mechanical law of equal action and reaction so successfully as a guide in commerce and industry that more than fifteen thousand individuals, banks and business organizations pay total fees approaching two million dollars annually for Mr. Babson's mathematical interpretation of equal action and reaction applied to the ebb and flow of the world's industry and trade.

The Babson Statistical Organization has become one of the greatest international forces for attainment of peaceful, scientific commerce, of practical secondary education and of world realization of the Golden Rule—which is the law of equal action in human relations.

How has Mr. Babson accomplished this? Simply by sticking to the supreme conviction that the law of equal action applies as completely to all human action as it does to the steam engine or dynamo. And by putting this conviction to the scientific research test of trying it upon a score of people, then upon a few hundred and now upon thousands, with the result that this law has become accepted by the hardest-boiled financiers and business executives, who pay liberally for this service of applied science and direct their mining, manufacturing, buying, and selling in accordance with the flow of the world's mental tide, accurately predicted and set down in Babson's nautical almanac of commerce.

FOUR OTHER LAWS THAT GOVERN HUMAN AFFAIRS have been brought to our attention, in addition to the law of equal action and reaction. We have often referred to them. They are of such extreme importance that we repeat them. They are:

1—That extreme specialization of the individual or nation (as in modern industry) which produce sincreased efficiency, leads to lack of adaptability; and that when specialization in any one direction goes so far as to unfit the organism for any condition of life except a single one, the chances of survival are greatly reduced and sooner or later the highly specialized organism becomes extinct or returns to a more generalized type.

2—That social or industrial specialization is destructive in accordance with this law of biology and evolution, unless, as in the social organization of the ants and bees, the specialization be correctly counterbalanced by complete social, industrial coöperation.