TITLE The Flotation Of Copper Silicate By Alkyl-Substituted Triphenyl Methane Dyes

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ABSTRACT OF THESIS

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"The Flotation of Copper Silicate by Alkyl-substituted Triphenyl Methane Dyes

Randall White Ludt

Certain alkyl-substituted triphenyl methane dyes are shown to act as collectors in the flotation of chrysocolla, a hydrated, partly colloidal, copper silicate mineral. Colloidal minerals have the property (1) of combining selectively with basic dyes of the triphenyl methane type. The attraction of crystalline minerals for these dyes is much less. This affords the basis by which chrysocolla can be separated from a quartz gangue.

Two types of substituted dyes are synthesized and used, namely: an alkyl-substituted malachite green type; and an alkyl-substituted rosaniline type.

The exact chemical structure of these dyes is considered secondary in importance to their property of causing the flotation of chrysocolla. Their structure is assumed on the basis of their properties as dyes, their method of preparation, and the intermediates used.

The malachite green type includes a homologous

alkyl-benzenes (2) (3) through the formation of a p-alkyl-phenyl-aldehyde (4). The aldehyde is then reacted with dimethyl aniline in a reaction,typical to the formation of the ordinary malachite green dye (5).

The dye called octyl-rosaniline is the only one of its type used. With octyl benzene as a reactant, o-nitro-octyl benzene (6) is formed and reduced to the amine (7). Aniline is then reacted with o-octyl aniline, in a typical dye-forming process, to form octyl-rosaniline (8).

The alkyl-substituted dyes are used as collectors in tests on a 100-gram flotation cell. A synthetic mixture of 1 gram of chrysocolla and 99 grams of gangue are considered as standard for the tests. It contains .235 percent copper. Pine oil is used as a frothing agent.

Results show that octyl-malachite green has possibilities for use as a commercial flotation agent. On a single flotation, a 64 percent recovery of copper is obtained when the assay in copper of the concentrate is increased eight to nine times. Either the percent recovery, or the assay of the concentrate can be increased, but at the expense of the other. The most successful tests are carried out at a pH of about 8, with a silica gangue. They show that the flotation is possible.

Because of clay mixed with the carbonate gangue, satisfactory separation can not be made from these materials. Tests on the other substituted dyes are less favorable than those on octyl malachite green.

Optimum conditions for the process are not determined. Satisfactory flotation takes place between rather narrow limits and is influenced by many factors. This investigation, by certain tests, does point out the need for further investigation. Among these important factors are the need of suitable depressants for not only colloidal minerals, such as clay, but also carbonate minerals and quartz; pH regulation with alkaline materials; the rate of addition of the collector; a further increase in the length of the substituted alkyl chain; and increase in the assay of the feed material.

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THE FLOTATION OF COPPER SILICATE BY ALKYL-SUBSTITUTED TRIPHENYL METHANE DYES

By

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ORGANIC PREPARATIONS

INTRODUCTION

Froth flotation is used for the separation and recovery of many minerals. The method is particularly well adapted to the recovery of the insoluble sulphides of metals, but is also extended to the separation of numerous other compounds. Some minerals, however, resist efforts toward satisfactory flotation. Among these is chrysocolla, a hydrated copper silicate.

The flotation operation requires the use of suitable reagents. In consideration of both experimental investigation and commercial ore dressing practice, it is evident that a new flotation agent, particularly applicable to chrysocolla, would have wide spread application.

PURPOSE AND SCOPE

The purpose of this investigation is to show that certain alkyl-substituted triphenylmethane dyes act as collectors in the flotation of chrysocolla.

Substituted dyes of both the malachite green and rosaniline types are used in the work. Three dyes of a malachite green homologous series are used. For identification, they are called butyl-malachite green, hexyl-malachite green, and octyl-malachite green. The single dye of the other type which is used is called octyl-rosaniline. Neither the preparation nor the use of these dyes is apparent in the literature. Their preparation is necessary. An outline of the procedure used for the preparation of these dyes is given in the appendix.

Certain conditions which influence the flotation results are investigated. The relative value of these substituted dyes as flotation agents is then determined on selected synthetic mixtures. Since chrysocolla is associated with commercial minerals of both acidic and basic nature, the tests are made with synthetic mixtures containing either silica or carbonates.

THE FLOTATION PROCESS

From the standpoint of the tonnage of ore treated, flotation is one of the most important of ore dressing processes. Relatively low grade ores can be economically treated. It is to be expected that the importance of flotation processes will increase with the decrease in the availability of rich ore.

Froth flotation had its beginning in 1906 when Sulman, Picard and Ballot (43) and likewise Chapman (8) applied violent agitation to an aqueous suspension of ore and caused a separation of minerals. Since that time development has been rapid. Many publications, among which are those by Taggert (45), Gaudin (28), Wark (49), Petersen (36), and DeWitt (17) clearly set forth both the principles and practice of froth flotation. It is carried out in an aqueous suspension of finely ground minerals into which air bubbles are introduced. Certain minerals have a greater attraction for the air bubbles than for the water and become attached to the bubbles. The mineral clad bubbles then rise to the surface and are skimmed off as a froth. An addition agent must be added to the cell to form a more permanent froth. Other reagents are usually added to aid in a better separation of ore and gangue. These reagents have the specific purpose of rendering the ore more, and the gangue less flotable.

Frothers

The purpose of a frother is to form a more or less stable froth on the surface of the pulp. Ore particles attached to the bubbles are thus drained from the cell with the froth.

They function by decreasing the surface tension. DeWitt (17) states that the frothing agent with the most negative slope of surface tension-molal concentration curve, in general, shows the greatest frothing power.

Structurally frothers are polar compounds composed of an oil soluble hydrocarbon group and a water soluble group. The oil soluble group may be an alkyl chain containing about ten carbon atoms. The water soluble group may be one such as the hydroxyl-, carboxyl-, aldehyde-, carbonyl-, amido-, or amino-group.

Some of the frothers commonly used are pine oil, eucalyptus oil, cresylic acid, terpineol, amyl alcohol, cresol, and soaps. The frother should not act as a collector. It should not be used in excess. It has a tendency to coat the ore particles to the exclusion of the collector and thus decrease flotation (24). The amount used as mentioned by Taggert (45) lies between .05 and .20 pounds per ton.

Collectors

Some minerals, among which are graphite and sulfur, inherently possess a surface which has an attraction for an air-water interface. These materials are collected by the rising air bubbles in a flotation cell. With the aid of a frother, they are carried from the surface as a concentrate.

Most minerals do not have this surface property. They are more easily wetted by water than by air. If, however, a hydrocarbon surface or film can be formed on the mineral, the particle then tends to be collected by the bubbles.

The function of a collector is to attach itself to the mineral and present an outward oily film to the air bubble. One end of the collector molecule contains an active polar group; the other end contains a hydrocarbon chain. The chemical structure of collectors is similar to that of frothers. The length of the hydrocarbon group on a collector which permits flotation, depends upon both the mineral to be recovered and upon the active polar group in the collector molecule. A xanthate collector may be effective with a methyl substituent; soap or an amino-collector may require a lauryl-group.

There are a great number of compounds that would serve as collectors but only relatively few are used commercially. The two general types of collectors used are negative or anionic reagents, and positive or cationic reagents.

The anionic reagents ionize into negative organic ions and positive metal or hydrogen ions. The organic anion can be considered to combine with the metal atom of the mineral. When the compound, assumed to be formed by the organic anion and the metal is insoluble, flotation can be expected. If this compound is soluble, poor collector action, if any, takes place.

Taggert (46) advances the idea that a compound is formed, and that adsorption of the collector on the mineral is of minor importance. Under these conditions, the mineral must be soluble enough to react with the collector but the product formed must still be insoluble.

Common anionic collectors are xanthates, mercaptans, thiophosphates, alkyl sulfates, alkyl sulfonates, aliphatic acid soaps, and fatty acids.

The cationic reagents form positive organic ions. This positive ion is formed either by the loss of a negative ion such as a bromide, or by the addition of a hydrogen ion, as in the case of amines. The positive organic ion then reacts with a negative ion of the mineral. This, as in the case of anionic reagents, results in a hydrocarbon film on the mineral surface.

Cationic reagents have an attraction for minerals of an acidic nature. They can be used to collect silicates and silica. Ralston (39) shows that a butyl amine will cause the flotation of talc, while a lauryl or stearyl amine is necessary for quartz.

Among the cationic reagents are alkyl pyridinium halides, quarternary ammonium compounds, and alkyl amines.

Activators

Heavy metal sulfides are quite readily caused to float by the use of a xanthate collector. The oxidized minerals do not have this property. The surface of many of these minerals can, however, be activated by the use of a suitable reagent, so that it is susceptible to the collector action.

Petersen (38) outlines the procedure for sulfidizing oxidized ores with alkali sulfides. When a suitable sulfide coating is formed, the mineral may be recovered by xanthate flotation. The sulfide of some metals, such as zinc, are themselves too soluble to respond to this treatment. Zinc blende, on the other hand, treated with copper sulfate, forms a surface of copper sulfide which is then amenable to xanthate flotation. The criterion for activation is the ability of the freshly formed surface to form an insoluble compound with the collector.

Depressants

When two minerals of a mixture are normally concentrated in the froth together, depressants can sometimes be used to restrict the flotation of one of them. The action of the depressants should be specific. Their concentration in the pulp must be closely governed because an excess may cause complete depression of the minerals.

Taggert (45) has classified the types of depressant action as follows:

1. Formation of an insoluble salt which is inactive to the collector. The heavy metals may form the hydroxide, carbonate or silicate. The alkaline earth metals may form the phosphates, silicates or fluorides.
2. Closure of the surface against collector action. The use of alkali sulfides may produce a surface which is too insoluble.
3. Nullification of the collector coating. A protective colloid may cover the surface.
4. Dispersion Gangue and slime particles may be dispersed by the presence of ions of higher valence.
5. Resurfacing to produce water-avidity. Hydrophilic colloids may coat the mineral particle.

Factors Influencing Cationic Flotation

The alkyl-substituted triphenyl methane dyes which are used in this investigation belong in the classification of cationic collectors. For this reason, factors which influence cationic flotation are stressed. In many cases, the observations apply to all flotation.

Particle Size

In the first place, the ore must be ground to such a fineness that particles of the valuable mineral are separated from the gangue. In the second place, the particles must be of sufficient fineness so that the bubble can raise them through the suspension. This depends to a great extent upon the specific gravity of the mineral. Thirdly, the particles must be small enough so that the hydrocarbon chains of the collector furnish sufficient bond with the air bubble.

In a survey of American flotation practice, Petersen (37) shows that the usual particle size varies between 50 and 100 microns. This corresponds to about 150- to 300-mesh.

When the particle size is decreased to below 5 microns, a slime is formed, which does not respond to flotation action. The slime may go to the interface and increase bubble toughness or because of its large surface area, it may use up an undue amount of collector. In flotation practice, removal of the slime is advisable.

Pulp Density

An increase in the apparent density of the pulp causes particles to rise to the surface more easily. Thus a higher concentration of minerals in the suspension tends to aid flotation but it also increases the harmful effects of slime. The usual amount of solids present in the pulp varies from 20 to 30 percent for optimum conditions.

Addition of Reagents

Reagents are usually added to the pulp in the order: conditioning agents; collector; and finally, frother.

Fahrenwald (24) shows that the frother contaminates the mineral surface, tending to exclude the collector. For this reason, it should ordinarily be added last and in small amounts.

For cationic collectors, the time and rate of addition of the reagent has an important influence on the flotation results. An excess concentration of cationic collector in the pulp at any time must be avoided. Wark and Wark (48) explain this phenominum by the formation of collector micelles at a certain critical concentration. Dean and Ambrose (11) suggest that since all cationic collectors are good emulsifying agents, an excess removes the water-repellant coating from the particles.

Dean and Ambrose (11) also offer data to show that a conditioning period for certain cationic agents may seriously decrease the extent of flotation. The reagent is more effective immediately after addition than any time later. Their data show that a 90 percent yield may be decreased to 10 percent by an 8 minute conditioning period before flotation.

Small changes in pH may have profound influence on the flotability of many minerals. Charts by Dean and Ambrose (13) show that silicate minerals and silica are generally recovered with cationic agents within a pH range of 6 to 8. At a pH of about 4, they are usually depressed. Hydrofluoric acid has the specific property of depressing quartz at a pH of 3 while allowing the flotation of feldspar.

Flotation of Gangue Materials

Since carbonates, silicates, and silica are encountered as gangue material, their action toward flotation procedure may be important in the use of the alkyl-substituted dyes as collectors. Most of these minerals can be removed from certain mixtures by present flotation procedure.

The carbonates are basic materials which quite readily combine with anionic or negative collectors. The Breerwood process (22) for adjusting the composition of cement rock is an example of the flotation of calcite from silicates and clay with a fatty acid as collector.

Data on the depression of limestone when using the cationic collector, lauryl pyridinium iodide, are given by Clemmer and Ambrose (9). Lactic acid, sodium silicate, sodium hydroxide, and copper sulfate all are shown to serve as depressing agents.

Quartz and silicates, on the other hand, are acidic materials which cannot be expected to combine directly with anionic collectors. They do, however, combine directly with the cationic positive-ion collectors. Ease of flotation depends upon the mineral but most of the silicates are more easily collected than is silica. Even with cationic reagents, quartz is found to be one of the most difficult to collect. It seems evident that when silicates such as clays are present in a mineral mixture, they should be removed before cationic reagents are applied to other minerals. This may be accomplished by flotation with short chain amines.

These gangue materials are all considered more flotable than chrysocolla by present practice. It would not be economically feasible to separate them from the ore mixtures and leave the chrysocolla in the tailings because the chrysocolla is present in such small amounts. The selection of a collector to remove a certain constituent is an economic problem. Other things being equal, it is advisable to cause the flotation of the material present in the smaller amount.

FLOTATION OF COPPER SILICATE

The most common copper silicate is known as chrysocolla. Doelter (20) states that chrysocolla is an aged gel which has become partly crystalline. Its formula is $CuSiO_2$, 2 H_2O. Compounds adsorbed on it are: CaO; MgO; ZnO; PbO; $CuCl_2$; and CO_2. It is often accompanied by malachite.

The amorphous or colloidal portion of the mineral, as is typical for colloidal minerals, contains a variable amount of water which is assumed to be adsorbed by the colloidal structure.

When the chrysocolla occurs with malachite, the malachite which is a copper carbonate may be recovered by flotation methods. The chrysocolla, however, is lost with the gangue. Barthelemy (3) gives an example of this type of process in which the gangue is a carbonate. Many of the ores contain a silica gangue.

Attempts to carry out the commercial flotation of chrysocolla are unsuccessful because the ordinary flotation agents do not selectively combine with it. It is by nature very hydrophilic and insoluble, and because of its water of hydration very non-flotable.

Previous Work on Chrysocolla Flotation

Work on the froth flotation of chrysocolla has been carried out in the United States Bureau of Mines

Laboratory work. In one of these processes, a xanthate collector (15) is used on the activated mineral; in the other, soap flotation (16) is used. Because of narrow ranges of application, the use of either of these processes is seriously restricted for commercial use. No references to the commercial flotation of chrysocolla have been found in the literature.

Xanthate Flotation of Chrysocolla

In the xanthate method (15) as developed by the Bureau of Mines, a synthetic mixture of chrysocolla and pegmatite (quartz, orthoclase with a little kaolin) is ground to pass a 100-mesh screen. Activation is carried out with either sodium sulfide or hydrogen sulfide in an aqueous solution at a pH of 4. The sulphidizing must be carried out within very narrow limits. An excess of sulphide acts as a depressing agent while too little sulphide causes poor recovery. When hydrogen sulphide is used, it is necessary to add the collector before the sulphidizing agent. The following charge gives a recovery of over 95 percent of the chrysocolla.

Head sample	.6% copper
Amyl xanthate	.2# per ton
Hydrogen sulphide	.2# per ton
Pine oil	as needed

Soap Flotation of Chrysocolla

The soap flotation of chrysocolla (16) is also accompanied by difficulties. The action of soap as a collector is not specific. The presence of heavy metal or alkaline earth ions causes the formation of insoluble soaps which are useless for the flotation of chrysocolla. The pulp must be regulated to a pH of 8 to 9 because free acid which is not a collector for chrysocolla forms in the acid range.

The sample is prepared from chrysocolla and pegmatite so that it passes through a 100-mesh screen.

Best results are obtained with soap as the only reagent. It acts as both a frother and a collector. The amount used varies with the composition of the pulp and ranges between 3 pounds per ton and 12 pounds per ton. Soaps of animal origin are more effective than of vegetable.

Alkyl-substituted Triphenyl Methane Dyes as Collectors

The structure of the alkyl-substituted triphenyl methane dyes seems to be very well suited to collector action on chrysocolla. Certain dyes, among which are malachite green and rosaniline, have a specific adsorption action for colloidal minerals. The principle is well known and used in many fields.

Endell (21) gives information on a method for the determination of the amount of colloidal material in clay by its selective adsorption of fuchsin.

The use of chromatrographic adsorption analysis is based on the same principle. Cain and Thorpe (7) suggest the separation of dyes by adsorption on kaolin. They list the dyes in the order of their preferential attraction to kaolin. Of the basic dyes, magenta, malachite green, methylene blue, and crystal violet are easily adsorbed, while the acid dyes in general, are not adsorbed.

Adsorption processes for the removal of colored compounds from aqueous solution are well known. The removal of polar compounds from petroleum oils and of colored material from syrup by adsorption processes, is a well developed science.

The results of some investigations on the adsorption of dyes by specific minerals are available. Suida (42) states that hydrated silicates are colored basic dyes. Dittler (19) shows that minerals with an acid reaction preferentially take up the basic dyes: fuchsin B; methane blue; and methyl green. Chrysocolla is one of these acid minerals. Acid violet is shown to be adsorbed by chrysocolla, but to a lesser degree. The colloidal structure is the determining factor; acid or basic reaction of the mineral is secondary. Dittler also relates that a calcined dye loses this characteristic for adsorbing dyes.

Crystalline material, such as quartz, is also colored by these dyes, but relatively more slowly and to a lesser degree. This is easily illustrated by placing both sand and chrysocolla in a dilute solution of crystal violet. France (26) reports tests to show that crystals do adsorb dyes and that different faces of the same crystal may have different adsorptive power for the same dye. Dean (16) shows that the dyes, crystal violet and toluidine blue, are taken up by quartz. The abstraction curves are of the adsorption type.

The adsorption of dyes by different types of material is one of degree. The mineral gels, however, have a greater attraction for dyes than crystalline solids. The taking-up of dyes by solids might be an adsorptive process or a chemical action. Freundlich and Neumann (27) regard the attachment of a dye to activated charcoal and certain mineral gels as being chemical in nature. In that case, the cation of the dye replaces a cation of the mineral gel, which can be assumed to be the hydrogen ion. Thus, the interchange of cations is the same as ordinarily takes place in dyeing cloth with a basic dye.

Regardless of the manner in which the dye becomes attached to the mineral, it is preferentially taken up by chrysocolla. It should be possible to use the active portion of the dye molecule as the active polar portion of a collector molecule. A long alkyl chain substituted into dye molecule should act as the non-polar end of the collector molecule.

The necessary length for such an alkyl chain is not known. As is previously noted, a methyl group may be of sufficient length on a xanthate collector, while a lauryl group may be necessary on an amine collector. It is known that the methyl group in the ordinary rosaniline dye does not effect the flotation. A longer alkyl chain is required. The alkyl-substituted dyes of the malachite green type which are used in this investigation, consequently, include the butyl-, the hexyl-, and the octyl-substituent.

Dyes of the alkyl-substituted triphenyl methane type may be expected to bring about flotation of not only chrysocolla but also of other colloidal or gel minerals. This may be an advantage in some cases but a disadvantage in others. The advantage lies in being able to concentrate other valuable gel minerals containing for example: copper; cobalt; nickel; and uranium; also to concentrate bauxite. The disadvantage lies in a lack of selectivity. Many of the copper silicate ores contain amorphous silicates such as clay in the gangue. These materials, however, might be removed by a preliminary flotation process.

Previous use of dyes as flotation reagents is reported by Taggert (45) from United States Patent 2,095,967. Certain acid and basic dyes are specified as depressants for molybdenite from copper sulphides. Among these dyes are methylene blue, aniline blue, Congo red, picric acid, acid green and acid blue.

PROCEDURE

Synthetic ore mixtures of chrysocolla and gangue are subjected to flotation tests. The collector action is found by a determination of the copper content of the concentrate as compared to that of the head mixture. The respective ore mixtures used are composed of chrysocolla and sand, and chrysocolla and dolomite. The limestone used in preliminary tests contains so many impurities that it is not used in the standard test procedure.

Preparation of the Sample

A relatively pure chrysocolla sample in massive pieces, up to six inches in length, is broken up in an iron mortor to sizes which pass a 20-mesh screen. The sample which does not pass the 20-mesh screen is further broken up in the mortor. The sample which passes the screen is classified according to size by a nest of standard screens. The screen sizes used are 60-mesh, 100-mesh, 150-mesh, and 200-mesh. Samples passing through the 100-mesh, 150-mesh, and 200-mesh screens are deslimed and used for preliminary tests.

The chrysocolla remaining on the 20-mesh, the 60-mesh, and the 100-mesh screens is ground wet in a pebble mill. It is then dried, screened, and deslimed for use in the standard tests.

Considerable clay is associated with the chrysocolla. It breaks up into very small particles and adheres to the chrysocolla particles. These clay particles would tend to form a slime during flotation. They are washed from the respective samples by repeatedly decanting the cloudy water suspension above the ore. This constitutes the desliming operation. Sizes prepared for flotation tests are: 100-150-mesh; 150-200-mesh; minus-200-mesh.

Samples of larger particle size prepared for preliminary flotation tests show relatively no tendency toward recovery. Consequently they are omitted from the standard procedure.

A copper analysis of the chrysocolla samples gives an average of 23.5 percent copper. Variation is within .2 percent.

Dolomite samples are prepared in a similar manner. The dolomite which is on hand in the laboratory in massive pieces is crushed first in a small jaw crusher, then subjected to wet pebble mill grinding, screening, and desliming. Desliming of the minus-200-mesh dolomite is carried further. About 130 grams are placed in the flotation cell with water and a frothing agent. The slime itself forms a copious froth and about 30 grams pass out with the froth. The dolomite sample is then drained from the cell, washed, and used in the test. The weight is determined by subtracting the dried weight of the slime.

The sand used is also on hand in the laboratory. It is relatively clean and white. Because of its relatively small size, it does not require preliminary crushing. It is immediately ground wet in the pebble mill, screened, and deslimed.

The synthetic ore mixtures for the respective tests are compounded from the deslimed material as needed. The standard test sample consists of 99 grams of gangue and one gram of chrysocolla. The standard ore mixture contains .235 percent copper. Ore mixtures of different copper content are used as noted.

Dean and Ambrose (41) suggest that the method of preparing the sample has an effect on flotation results. The surface of a sample from wet pebble mill grinding should be cleaner than the surface of dry-ground material. Being cleaner, it has a greater tendency to combine with the reagents and thus a greater tendency to be collected. In this investigation, samples from dry grinding have been used for the preliminary tests.

The Flotation Cell

The flotation cell is a 100-gram batch unit, provided with an air inlet at the bottom, immediately above which is a variable speed agitator. The agitator and shaft are made of steel, the cell itself of Lucite. (See Fig. 1.)

Froth discharges into a Buchner funnel where the concentrate is collected on a filter paper. The liquid is drawn through the funnel and into a glass bottle by vacuum. It is drained into a second bottle and fed continuously back to the cell at a rate of a little over

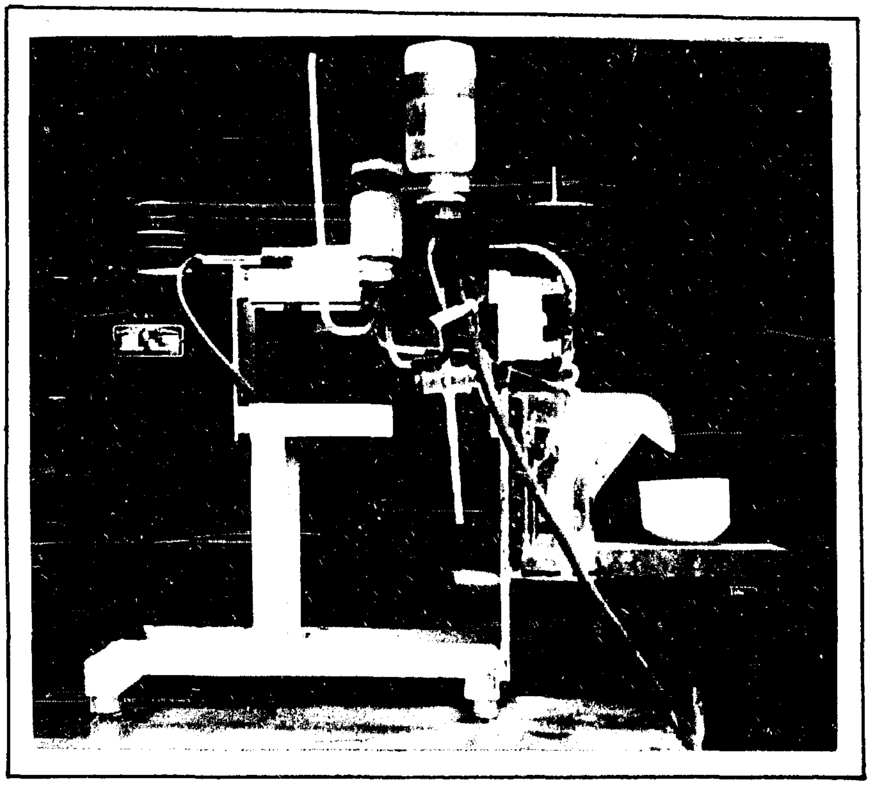


Fig. 1. Flotation Cell

one drop per second. This regulates the rate at which the froth leaves the cell.

The total pulp charge to the cell consists of 100 grams of ore mixture and 300 grams of water. A variable amount of this water, depending upon froth depth in the cell, is in the bottles outside the cell.

Collector Solution

The alkyl-substituted triphenyl methane dyes are used for collectors. They are dissolved in ethanol-water mixtures in a concentration of .1 gram per 100 cc. The percentage of alcohol used varies with solubility of the dye. A 50 percent alcohol solution is used for butyl- and hexyl-dyes; a 70 percent solution for octyl-malachite green; and 95 percent alcohol for octyl-rosaniline.

Operation of the Cell

The agitator and air pump are started. About 150 grams of water, then the gangue and the chrysocolla are put into the cell. About 50 grams of water are drawn into the water supply bottle. The rest of the 300 grams of water is run into the cell. Modifying agents, if any, are added, and the pulp is allowed to mix for 15 minutes. Pine oil, as needed, is added on the end of a fine wire. An excess must be avoided. The collector is then added by stage addition over the period of the run. The collector solution is added slowly from a pipette which is inserted well down into the pulp, in quantities of .5 cc. When added to the top of the pulp, the froth picks up the collector and carries it over immediately. Filter papers may be changed to obtain more detailed information on a run.

At the end of the run, the pulp is drained from the cell and a sample is taken for pH measurement on a Beckman meter. The filter paper holding the concentrate is dried and weighed to obtain the weight of concentrate. The percentage of copper is then determined in the concentrate.

Flotation Results

In this investigation only single flotation tests are run on a given quantity of ore. The concentrate might be further enriched by an additional flotation operation. In commercial practice, the ore is treated in a series of operations. The pulp goes first to a rougher cell where the first separation is made. The tailings from the rougher cell are subjected to further flotation in a scavenger cell. The concentrate from the rougher cell goes to a cleaner cell where a higher concentration of the desired mineral is obtained. Thus in a series of flotation actions, both the percentage recovery and the enrichment of the product may be increased over what might be obtained in a single flotation process.

Composite runs are made in many of the main tests when detailed information is desired. The collector is added at a given rate during the entire test, but the filter paper holding the concentrate is replaced at designated intervals. In this way data can be obtained on the effect of the addition of various amounts of collector. In calculating the results, the total amount of concentrate which has been floated from the beginning of the test is included with that of a given period.

Determination of Copper

Copper is determined by the method of Park (35). A sample containing not more than .2 grams of copper is dissolved in nitric acid and boiled down to about 5 cc. It is then diluted to about 30 cc. and boiled in order to expel the oxides of nitrogen and insure solution of material. When dark colored residue is present, the solution is filtered and the residue washed with dilute nitric acid. The solution is neutralized with ammonia, but an excess is avoided. Two grams of ammonium bifluoride are added and shaken with the solution. One gram of potassium biphthalate is likewise added and then

3 grams of potassium iodide. The solution is then titrated with N/10 sodium thiosulphate solution. Starch is used as an indicator.

TABULATED RESULTS

TABLE 1.

Flotation Action

Mineral mixture: 100 gm. sand-chrysocolla

Particle size: minus-200-mesh

pH: 7.7 - 8.3

Exp. No.	Collector Dye	Collector # ton	Heads % Copper	Time Min.	Concentrate % Copper	Concentrate % Recovery	Concentrate #Dye / #Copper
39	Octyl-rosaniline	.04	.235	4	1.17	14.5	.059
	Alkyl-malachite green						
32	Butyl-	.04	.235	8	.59	17.0	.072
31	Hexyl-	.03	.235	6	1.01	41.1	.016
36	Octyl-	.12	.235	10	2.0	64.0	.040
46	Octyl-	.28	.705	21	2.9	62.1	.032

TABLE 2.

Effect of Particle Size

Collector: .03 #/ton hexyl-malachite green

Mineral mixture: 100 gm. sand-chrysocolla, .235% copper

Exp. No.	Mesh	Min	pH	Concentrate Grams	Concentrate % Copper	Concentrate % Recovery
4	150-200	2	7.8	1.40	.63	3.73
5	-200	3	7.8	2.49	1.07	11.25

TABLE 3.

Effect of Rate of Collector Addition

Exp. No.	Collector		Time	Rate	Concentrate	
	Dye	# ton	Min.	Grams Min.	% Copper	% Recovery
5	Hexyl-malachite	.03	3	.00050	1.07	11.25
31-C	Hexyl-malachite	.03	6	.00025	1.01	41.1
36-A	Octyl-malachite	.03	2	.00075	2.25	17.4
34-C	Octyl-malachite	.03	6	.00025	1.43	28.5
36-B	Octyl-malachite	.06	4	.00075	2.4	34.8
34-F	Octyl-malachite	.06	12	.00025	1.46	53.0

TABLE 4.

Action of Butyl-malachite Green

Collector: butyl-malachite green

Mineral mixture: 100 gm. sand-chrysocolla, .235% copper

Frother: pine oil

Exp. No.	Mesh	Agent	Dye # ton	Min.	pH	Concentrate		
						Grams	% Copper	% Recovery
15	150-200	HF	.03	7	4.3	2.34	nil	
16	150-2--	HF	.024	8	4.1		trace	
32-A	-200		.01	2	8.3	2.23	.74	6.9
32-B	-200		.02	4	8.3	3.79	.70	11.1
32-C	-200		.03	6	8.3	5.61	.60	14.3
32-D	-200		.04	8	8.3	6.85	.59	17.0
32-E	-200		.05	10	8.3	8.55	.54	19.6

Mineral mixture: 100 gm. dolomite-chrysocolla,

.235 % copper

Exp. No.	Mesh	Agent	Dye #/ton	Min.	pH	Concentrate Grams	Concentrate % Copper	Concentrate % Recovery
12	-200		.054	3	7.8	3.52	trace	
33-A	-200	$Al_2(SO_4)_3$ .4#/ton	.01	2	7.9	2.08	trace	
33-G	-200	$Al_2(SO_4)_3$ .4#/ton	.08	18	7.9	11.63	trace	

TABLE 5

Action of Hexyl-malachite Green

Collector: hexyl-malachite green

Mineral mixture: 100 gm. sand-chrysocolla, .235% copper

Frother: pine oil

Exp. No.	Mesh	Agent	Dye #/ton	Min.	pH	Concentrate Grams	Concentrate % Copper	Concentrate % Recovery
4	150-200		.028	2	7.8	1.40	.63	3.73
5	-200		.03	3	7.8	2.49	1.07	11.25
10	-200	HCl	.03		2.3	12.24	nil	
28-A	-200	HF	.02	2	4.1	3.49	.02	.3
28-B	-200	HF	.03	3	4.1	10.09	.18	8.4
30-A	-200	HF	.01	2	4.0	1.52	.09	.6
30-B	-200	HF	.02	4	4.0	5.31	.21	4.9
30-C	-200	HF	.03	6	4.0	9.61	.18	7.5
37	-200	H_2SO_4	.11	4	4.7	12.71	.05	2.5

Exp. No.	Mesh	Agent	Dye #/ton	Min.	pH	Concentrate Grams	Concentrate % Copper	Concentrate % Recovery
31-A	-200		.01	2	7.9	2.50	.99	10.6
31-B	-200		.02	4	7.9	4.99	1.08	23.0
31-C	-200		.03	6	7.9	9.51	1.01	41.1
31-D	-200		.04	8	7.9	15.45	.75	49.5
31-E	-200		.05	10	7.9	22.45	.61	59.3
31-F	-200		.06	12	7.9	28.35	.50	60.9
31-G	-200		.08	14	7.9	39.25		

Mineral mixture: 100 gm. sand-chrysocolla, .47 % copper

Exp. No.	Mesh	Agent	Dye #/ton	Min.	pH	Concentrate Grams	Concentrate % Copper	Concentrate % Recovery
27	-200	HF	.05	2	4.1	4.61	.77	7.5
A17	-200	HF citric acid .5#/ton	.016	6	3.6	2.08	.62	2.6
A13	-200	HCl	.01	5	4.0	1.75	1.17	4.4
A13-B	-200	HCl	.02	10	4.0	5.03	.99	10.7

Mineral mixture: 100 gm. dolomite-chrysocolla,

.235 % copper

Exp. No.	Mesh	Agent	Dye #/ton	Min.	pH	Concentrate Grams	Concentrate % Copper	Concentrate % Recovery
A4	-150		.02	7	7.2	30.2	(not deslimed)	
1	-200	Na_3PO_4 .5#/ton	.014	6	8.2	4.51	.14	2.7

Exp. No.	Mesh	Agent	Dye #/ton	Min.	pH	Concentrate Grams	Concentrate % Copper	Concentrate % Recovery
2	-200	$Al_2(SO_4)_3$ .32#/ton	.014		7.0	5.67	.28	6.8
3	-200	sodium silicate .4#/ton	.014		7.0		nil	
8-A	-200	acetic acid 4.2#/ton	.04	3	7.4	11.97	nil	
8-B	-200	acetic acid 4.2#/ton	.062		7.4	19.61	nil	
6	150-200		.03	3	7.4	5.16	nil	

Mineral mixture: 100 gm. dolomite-chrysocolla,

.47 % copper

Exp. No.	Mesh	Agent	Dye #/ton	Min.	pH	Concentrate Grams	Concentrate % Copper	Concentrate % Recovery
25-A	-200		.06	1		9.58	.22	4.5
25-B	-200		.12	2.5		14.33	.26	7.9

TABLE 6.

Action of Octyl-malachite Green

Collector: octyl-malachite green

Mineral mixture: 100 gm. sand-chrysocolla, .235 % copper

Frother: pine oil

Exp. No.	Mesh	Agent	Dye #/ton	Min.	pH	Concentrate Grams	Concentrate % Copper	Concentrate % Recovery
36-A	-200		.03	2	8.1	1.82	2.25	17.4

Exp. No.	Mesh	Agent	Dye #/ton	Min.	pH	Concentrate Grams	% Copper	% Recovery
36-B	-200		.06	4	8.1	3.38	2.4	34.8
36-C	-200		.09	7	8.1	5.32	2.2	52.2
36-D	-200		.12	10	8.1	7.52	2.0	64.0
36-E	-200		.14	12	8.1	10.06	1.7	74.0
36-F	-200		.17	14	8.1	11.59	1.54	76.5
34-A	-200		.01	2	8.0	1.12	1.27	6.5
34-B	-200		.02	4	8.0	3.24	1.35	18.6
34-C	-200		.03	6	8.0	4.68	1.43	28.5
34-D	-200		.04	8	8.0	6.20	1.43	37.8
34-E	-200		.05	10	8.0	7.80	1.47	48.5
34-F	-200		.06	12	8.0	8.55	1.46	53.0
43-A	-200	HCl	.03	2	6.6	2.02	1.2	10.3
43-B	-200	HCl	.06	5	6.6	4.11	1.11	19.5
43-C	-200	HCl	.09	7	6.6	5.94	1.15	29.1
43-D	-200	HCl	.12	10	6.6	9.36	.96	38.3
43-E	-200	HCl	.15	12	6.6	12.43	.88	46.6
43-F	-200	HCl	.18	15	6.6	14.84	.83	52.5
47-A	-200	Na_2CO_3 .8 #/ton	.04	3	8.1	.58	2.6	6.4
47-B	-200	Na_2CO_3 .8 #/ton	.08	6	8.1	1.02	3.1	13.6
47-C	-200	Na_2CO_3 .8 #/ton	.12	9	8.1	1.88	3.1	24.5
47-D	-200	Na_2CO_3 .8 #/ton	.16	12	8.1	4.36	2.5	45.0

Exp. No.	Mesh	Agent	Dye # ton	Min.	pH	Concentrate Grams	% Copper	% Recovery
47-E	-200	Na_2CO_3 .8 #/ton	.20	15	8.1	7.48	1.8	58.0
47-F	-200	Na_2CO_3 .8 #/ton	.24	18	8.1	11.01	1.47	70.0

Mineral mixture: 100 gm. sand-chrysocolla, .705 % copper

Exp. No.	Mesh	Agent	Dye # ton	Min.	pH	Concentrate Grams	% Copper	% Recovery
46-A	-200		.04	3	7.7	1.67	3.84	9.1
46-B	-200		.08	6	7.7	2.62	3.87	14.4
46-C	-200		.12	9	7.7	3.88	4.14	22.7
46-D	-200		.16	13	7.7	6.48	3.98	36.6
46-E	-200		.20	16	7.7	8.35	3.74	44.4
46-F	-200		.24	19	7.7	10.61	3.41	51.5
46-G	-200		.28	21	7.7	15.09	2.90	62.1
46-H	-200		.32	24	7.7	21.31	2.42	73.2

Mineral mixture: 100 gm. dolomite-chrysocolla

.235 % copper

Exp. No.	Mesh	Agent	Dye # ton	Min.	pH	Concentrate Grams	% Copper	% Recovery
40-A	-200	$Al_2(SO_4)_3$ .4 #/ton	.04	2	8.0	5.79	.16	4.26
40-B	-200	$Al_2(SO_4)_3$ .4 #/ton	.28	16	8.0	18.68	.05	4.25

TABLE 7.

Action of Octyl-rosaniline

Collector: octyl-rosaniline

Mineral mixture: 100 gm. sand-chrysocolla, .235 % copper

Frother: pine oil

			Dye			Concentrate		
Exp. No.	Mesh	Agent	# ton	Min.	pH	Grams	% Copper	% Recovery
38-A	-200		.04	2	8.0	5.34	.60	13.6
38-B	-200		.08	4	8.0	12.53	.34	18.2
39-A	-200		.02	2	8.3	1.82	.99	7.6
39-B	-200		.04	4	8.3	4.50	1.17	14.5
39-C	-200		.05	6	8.3	7.23	.60	18.3

Mineral mixture: 100 gm. dolomite-chrysocolla, .235 % copper

			Dye			Concentrate		
Exp. No.	Mesh	Agent	# ton	Min.	pH	Grams	% Copper	% Recovery
42	-200	$Al_2(SO_4)_3$ .38 #/ton	.19	15	8.0	6.19	.37	8.1

COMPARISON OF DYES AS COLLECTORS

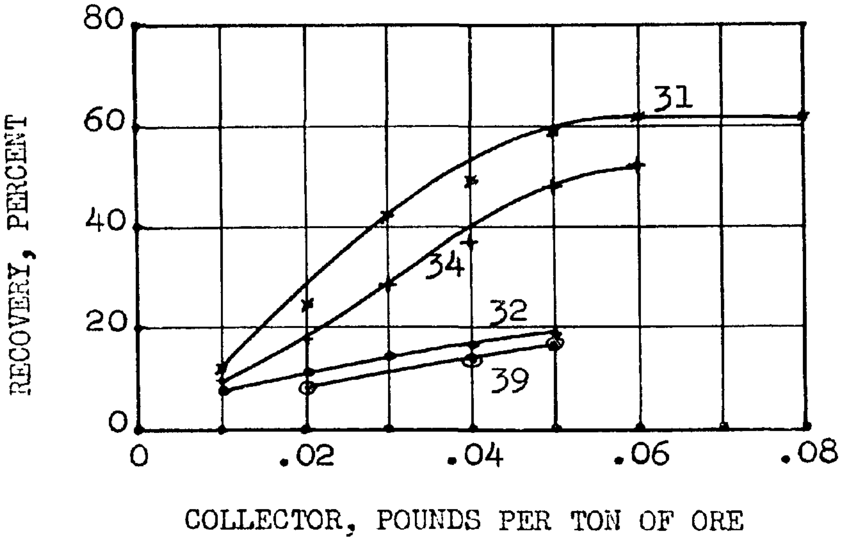


CHART 1. Recovery of Chrysocolla

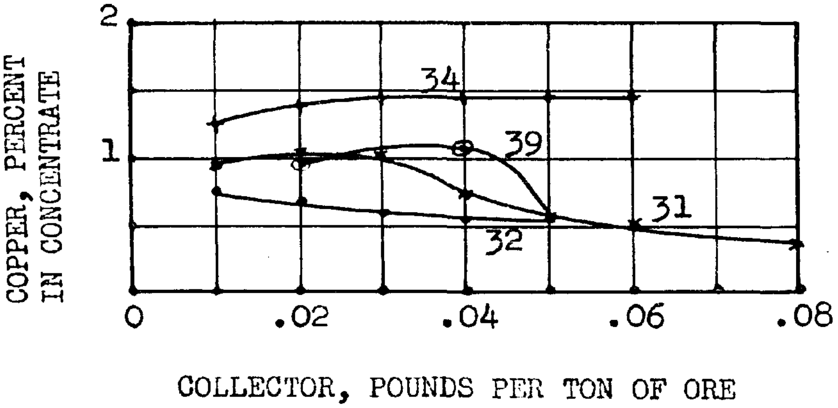


CHART 2. Assay of Concentrate

Feed mixture: 100 gm. sand-chrysocolla, .235 % copper

Exp. No.	Collector	pH	Grams dye/min.
32	Butyl-malachite green	8.3	.00025
31	Hexyl-malachite green	7.9	.00025
34	Octyl-malachite green	8.0	.00025
39	Octyl-rosaniline	8.3	.0004

EFFECT OF RATE OF COLLECTOR ADDITION

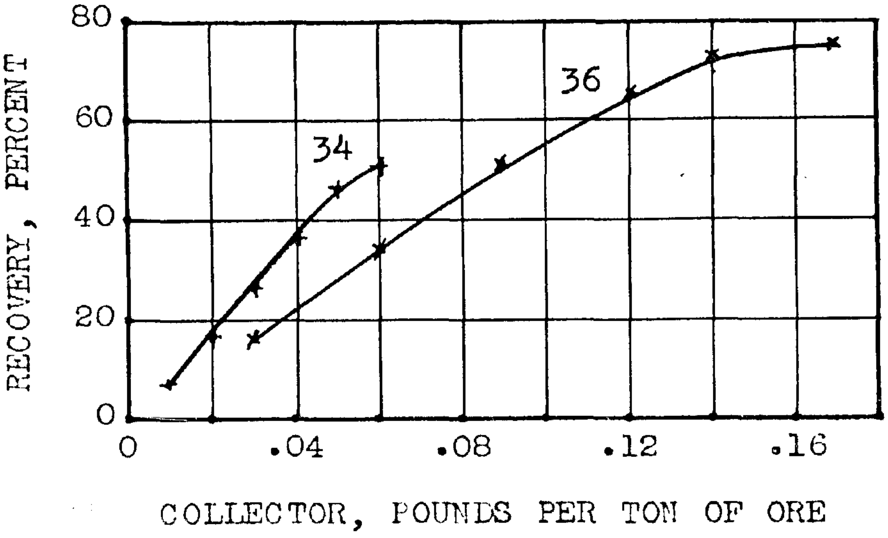


CHART 3. Recovery of Chrysocolla

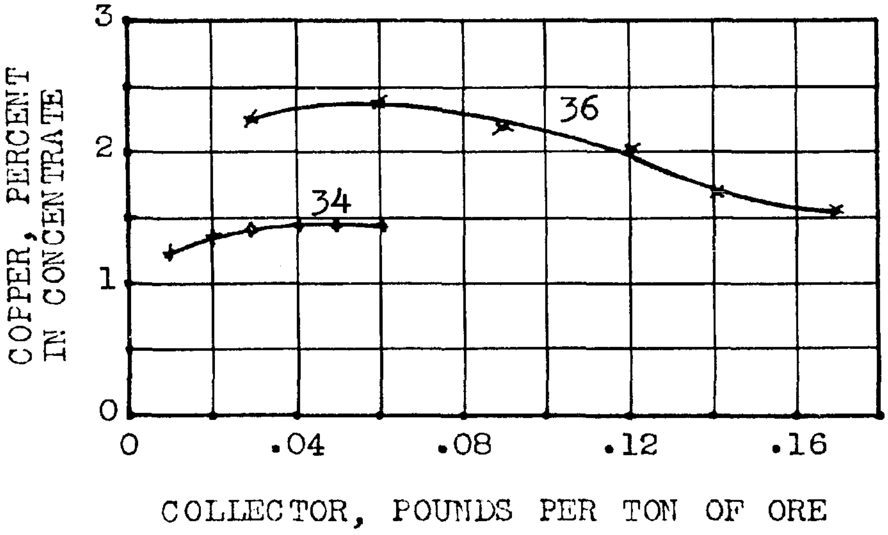


CHART 4. Assay of Concentrate

Collector: octyl-malachite green

Mineral mixture: 100 gm. sand-chrysocolla, .235 % copper

Exp. No.	Grams dye/min.	# dye/# copper
34	.00025	.024
36	.00061	.05

EFFECT OF ENRICHED FEED MATERIAL

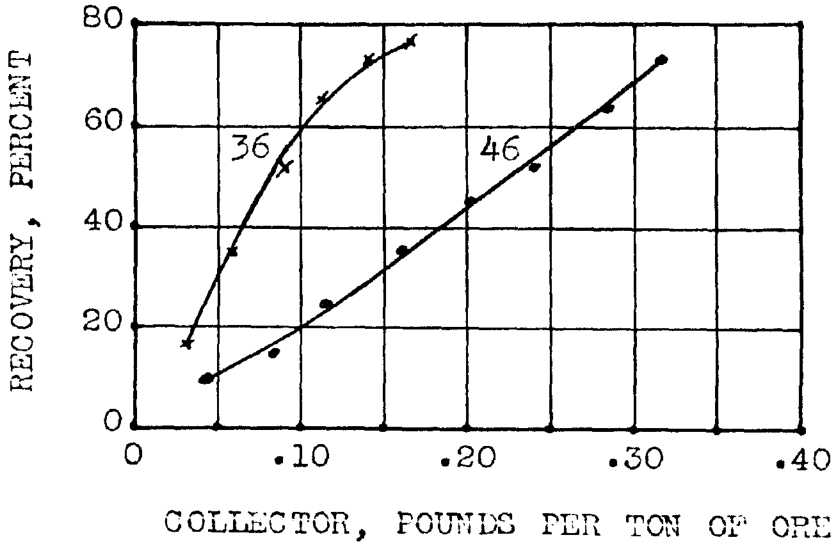


CHART 5. Recovery of Chrysocolla

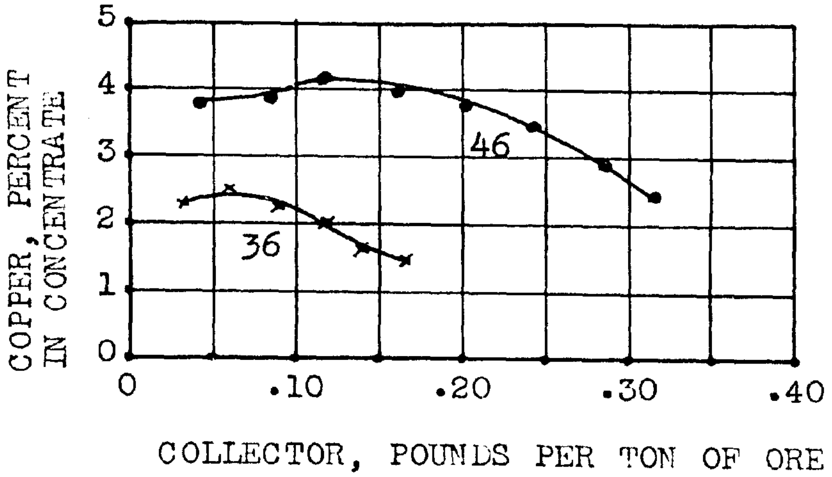


CHART 6. Assay of Concentrate

Collector: octyl-malachite green

Exp. No.	Heads % Copper	Grams dye/min.	# dye/# copper
36	.235	.0006	.040
46	.705	.0006	.032

EFFECT OF ADDITION AGENTS

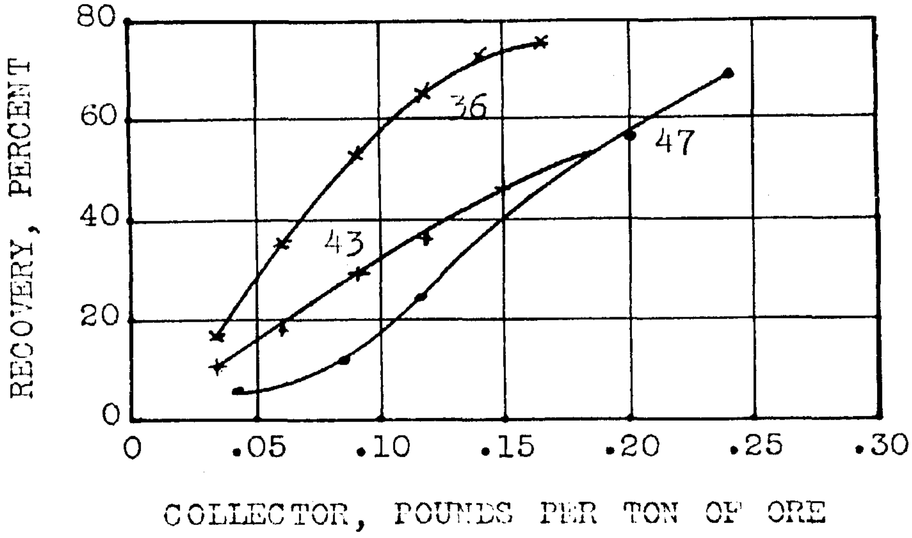


CHART 7. Recovery of Chrysocolla

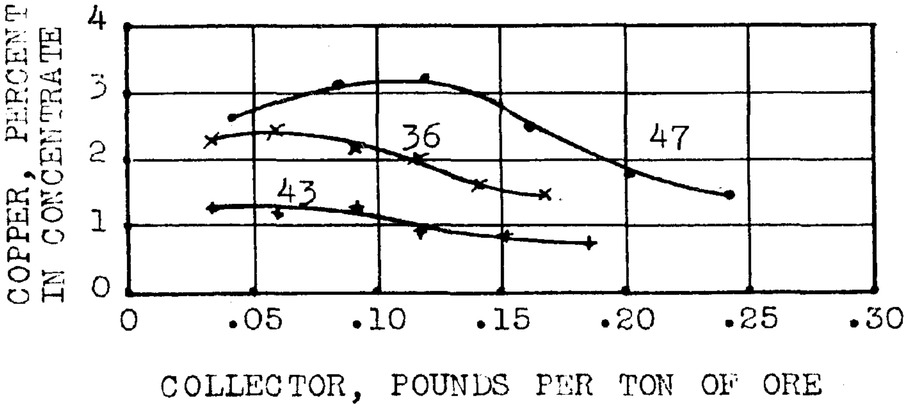


CHART 8. Assay of Concentrate

Collector: octyl-malachite green

Exp. No.	Agent	pH	Grams dye/min.
36		8.1	.00061
43	HCl	6.6	.00061
47	Na_2CO_3, .8 #/ton	8.1	.00067

DISCUSSION OF RESULTS

As previously stated, the primary purpose of this investigation is to show that alkyl-substituted triphenyl methane dyes cause the flotation of chrysocolla. The results, as summarized in Table 1, clearly show that they do this, and that one of those used, octyl-malachite green, has possibilities toward use as a commercial flotation agent.

Optimum conditions for operation are not determined. Extended investigation on the primary requirements for flotation shows only a limited number of details. The range of variables is great and certain slight variations in conditions are shown to have a profound influence on the percentage recovery, and the percentage copper in the concentrate.

The investigation does show trends in the influence of certain variables on flotation action and it does open up many questions with regard to economical commercial use. Many of these questions could be answered by extended laboratory work.

When these dyes are used as collectors, they first dye certain solid material in the pulp. The dyed material, be it ore or gangue, has the tendency to float. During the early part of the run, that material which has the greatest attraction for the dye will tend to be collected. Any colloidal material, such as slime, or a colloidal mineral, such as chrysocolla or clay, has a greater attraction for the dye than does quartz or limestone.

Successful flotation of chrysocolla can not be expected when the charge to the cell contains large amounts of other colloidal material. The samples of dolomite and of limestone used in the tests have an aluminum content which appears to be clay. Unsatisfactory separation of chrysocolla from dolomite or limestone gangue is attributed to the presence of this clay.

Toward the end of a run, the continued presence of dye in contact with the crystalline material, and the excess of dye present in the pulp, cause the non-colloidal material to float. Whenever an excess of dye is used in the tests, the tailings at the end of the run are more or less colored.

An important problem with regard to the flotation of chrysocolla with the alkyl-malachite green dyes is the selection of a specific depressing agent for the gangue material. This is true for not only dolomite and clays but also for silica. It is undoubtedly possible to separate the clay by a preliminary flotation with a cationic collector. If the colloidal material were present in small quantities, this would be feasible. If it were present in large quantities, the use of a satisfactory depressing agent seems to be the only reasonable solution.

Accuracy of Results

The conclusions drawn from these tests should be considered as trends and not as specific numerical relationships. Comparisons can be made, however, on a general basis in spite of the great number of factors which influence flotation results.

The values for pH measurement should be considered as approximate. The sample for pH measurement is taken at the end of a composite run and is recorded for the entire run. During the test, increasing amounts of collector are added, which can be expected to change the pH value to a slight extent.

Particle Size

The mineral mixtures on many of the preliminary tests range in size from 30-mesh to 100-mesh. Practically no flotation action is observed until the size is decreased to about 200-mesh.

A comparison of the flotation action of hexylmalachite green on a sand-ore mixture of 150-mesh to

200-mesh, and of minus-200-mesh is obtained from Table 2. Sizes smaller than 200-mesh are much more easily collected and the concentrate yields a higher percentage of copper. For good recovery the particle sizes must be smaller than 200-mesh.

The minus-200-mesh mixture is well within the limits of common milling practice. As Petersen (37) shows, the usual commercial sizes vary between 150-mesh to 300-mesh.

Butyl-malachite Green

Butyl-malachite green has some collector action on chrysocolla but the extent of this action is not great. Data on this collector action are found in Table 4. Its relative attraction for silica is large. With only 17 percent recovery of the copper, the concentrate is composed of 97.5 percent sand. This is equivalent to an enrichment in the concentrate of only 250 percent.

When the pulp is made acid with hydrofluoric acid to a pH of about 4, very little, if any flotation of chrysocolla occurs. The chrysocolla is depressed while sand is carried over in the concentrate.

The flotation action of butyl-malachite green is not evident when dolomite is used as the gangue. Clays which are present in the dolomite are apparently separated to the exclusion of the chrysocolla. Some indication of flotation of the chrysocolla is obtained when aluminum sulfate is used as a depressant, but the recovery of copper amounts only to a trace. The presence of clay in the concentrate is apparent from the large amount of aluminum hydroxide formed during the chemical analysis.

Hexyl-malachite Green

Appreciable recovery of chrysocolla is obtained when hexyl-malachite green is used as a collector. Data on this flotation action are given in Table 5. With sand as the gangue, a 40 percent recovery of copper is obtained with an enrichment of the concentrate of 430 percent. This is equivalent to 96.7 percent sand in the concentrate as compared to 99 percent in the head sample. A recovery of the copper up to 60.9 percent can be obtained, but this is at the expense of the percentage copper in the concentrate.

When either hydrochloric acid or hydrofluoric acid is used to lower the pH to about 4, a depression of both sand and chrysocolla occurs. The hydrofluoric acid seems to depress the chrysocolla to a greater extent than the sand.

The use of sulfuric acid, decreasing the pH to 4.7, almost completely depresses the chrysocolla, while allowing flotation of the sand. Citric acid with hydrofluoric acid at a pH of 3.6 has an effective depressing action on both sand and the chrysocolla.

Separation of the chrysocolla from dolomite-chrysocolla mixtures is ineffective either with or without the commonly used depressants for dolomite. Even though the dolomite used is deslimed, the presence of colloidal aluminum minerals interferes with the chrysocolla flotation.

Some flotation of chrysocolla is obtained when depressants are not used, but the concentrate is not enriched in copper above the composition of the head sample. The use of aluminum sulfate, as a reagent, likewise allows some flotation without enrichment.

The common depressants for dolomite, such as tricalcium phosphate, sodium silicate, and acetic acid, all depress the chrysocolla. The two latter compounds do not allow the flotation of any chrysocolla under the conditions of these tests.

When flotation is attempted with the dolomite gangue, without previous desliming, about one third of the entire mineral charge goes over in the froth. This is shown in Table 5, Test A-4. This quantity may be easily removed before flotation tests by subjecting the dolomite to the action of the flotation cell.

Octyl-malachite Green

Results on the flotation of chrysocolla from sand with octyl-malachite green, shown in Table 6, indicate that the process may be commercially feasible. In the regular test runs with 1 percent chrysocolla in the head material, 64 percent of the copper can be recovered with an enrichment of 850 percent. When a richer head material, 3 percent chrysocolla is used, the recovery is 73 percent with an enrichment of 410 percent. These values vary with the amount of collector used.

The presence of hydrochloric acid, resulting in a decreased pH, decreases both the percentage recovery and the enrichment. The results indicate that a pH of about 8 is desirable. When the pH is lowered to 6.6 with hydrochloric acid, the relative tendency for silica to pass over in the froth is greatly increased.

Sodium carbonate is found to act as a stronger depressant for silica than for chrysocolla. By using larger amounts of collector, a concentrate with higher percentage of copper may be obtained, but the ultimate yield is less. The use of sodium carbonate gives results which appear promising.

Flotation of chrysocolla from the dolomite is not satisfactory. The aluminum sulfate used for a depressant prevents the flotation of chrysocolla.

Octyl-rosaniline

Definite flotation of chrysocolla is observed when octyl-rosaniline is used as a collector with a sand-chrysocolla ore mixture. The results are shown in Table 6. Both percentage recovery and enrichment of the concentrate are small. With 14.5 percent recovery, enrichment is about 500 percent.

This dye is different than the others both in the number of amino-groups, the type of amino-group, and the location of the alkyl-chain. The smaller flotation effect obtained with octyl-rosaniline may be due to any or a combination of these differences. It is possibly due to the presence of primary amino-groups as compared to the tertiary groups which are present on the alkyl-malachite green type of dyes.

Although both recovery and enrichment is very poor when octyl-rosaniline is used as a collector, they appear better than for any of the others when used with the dolomite gangue. The total recovery of copper is 8.1 percent while the enrichment is about 160 percent. However, a very large amount of the collector is used.

Length of the Alkyl-Chain

Comparison can be made with respect to the effects of the alkyl chain length on the flotation properties of the malachite green type of compound by reference to Charts 1. and 2. These charts do not show the best results that have been obtained for octyl-malachite green. They show a comparison at the same rate of addition of collector for each reagent.

The dyes with the longer alkyl-chains have relatively better collector properties. Assay of the concentrate shows greater enrichment. A greater ultimate percentage recovery is also obtained.

The hexyl-malachite green appears to have greater reactivity per unit weight than the octyl-malachite green. This might be due to a greater molal concentration or it might also be due to the relative induction period required by each. With a satisfactory depressant for silica, the hexyl-malachite green should be a suitable collector.

Under the present flotation conditions, the octyl-malachite green is the only dye which suggests economical commercial use. The use of a longer substituted chain on the dye molecule could be expected to accentuate the difference found between the hexyl- and octyl-compounds. As with other collectors, an optimum chain length can be expected to exist. Chain lengths greater than the optimum usually decrease in effectiveness due to the decreased solubility of the compound. The use of a still longer chain length for the substituent is suggested for future work.

Octyl-rosaniline yields very poor results in comparison to the other dyes. By a selection of more suitable conditions, however, its effectiveness could undoubtedly be improved. The rate of collector addition is not the same for octyl-rosaniline as for the others to which it is compared, but this difference should not be expected to appreciably change the relative results.

Rate of Addition of the Collector

A comparison of the effect of the rate of addition of the collector may be obtained by reference to Table 3. and to Charts 3. and 4. The comparison may be based either upon flotation results per unit weight of collector used, or upon the ultimate yields.

In Table 7. a comparison is made, based upon a given amount of collector used. The faster rate of addition gives a concentrate which is richer in copper but it also gives less percentage recovery. The longer time allowed with the lower rate gives the sand an opportunity to be dyed by the collector. Thus with the different rates of addition used, the assay of the concentrate may increase over 60 percent but the percentage recovery may decrease 35 percent.

A more significant comparison can be made on the basis of the ultimate yields as indicated in Charts 3.

and 4. By using a higher rate of addition, both the assay of the concentrate and the percentage ultimate recovery are increased. About twice as much collector is used at the faster rate, in order to recover the same amount of copper. The question of optimum rate of addition involves an economic balance in which the value of the recovered ore and the cost of the collector must be taken into consideration.

All tests are run at an approximately constant rate of collector addition for the test. This seems to build up an excess of collector in the pulp. An alternate method of adding the collector at a variable rate might prove of advantage and should be the problem of a future investigation.

Amount of Chrysocolla in the Head Charge

The standard tests are carried out with 1 percent of impure chrysocolla in the feed to the flotation cell. The copper content is .235 percent. This is below the percentage that might be expected in commercial practice.

Results when using a larger percentage of copper in the feed material are shown in Charts 5. and 6. and in Table 1. A head sample of .705 percent copper is used to show this effect. The rates of addition of the dye cannot be considered comparable. Comparison shows that flotation of chrysocolla in the early part of the run depends upon the amount of collector added. Approximately an equal weight of ore is floated in the first 14 minutes in each test when about an equal amount of collector is added. The chrysocolla is carried over in the froth at a somewhat increased rate after this initial period but the amount of sand accompanying it increases in greater proportion.

The percentage recovery on both tests is about the same. The percentage enrichment of the concentrate is greater when the feed with a low assay value is used. Adjustment in rates of collector feed could easily make either more or less difference between them.

Use of collector per pound of copper compound floated is 25 percent lower when the richer feed is used.

On the basis of these limited data, and the effect of the factors already considered, it is justifiable to assume that flotation practice with an enriched head material would be more successful than with a leaner mineral mixture.

Addition Agents

The depressing agents used in these tests do not show satisfactory results. Sodium silicate and acetic acid both seem to completely depress chrysocolla. Trisodium phosphate and aluminum sulphate show no improvement in the assay of the concentrate. Hydrofluoric acid and hydrochloric acid depress chrysocolla to a greater extent than sand but allow limited recovery.

The use of sodium carbonate with a sand-chrysocolla mineral mixture offers some possibilities. It depresses both sand and chrysocolla and requires more collector. However, it does permit considerably increased percentage copper in the concentrate. Comparison of the use of sodium carbonate and hydrochloric acid are shown in Charts 7 and 8. The rates of collector addition are about equal for the three tests.

If advantage is to be taken of the use of sodium carbonate, a low yield is indicated. At a recovery of less than 50 percent, the assay of the concentrate can be maintained at about 2 percent copper. Under these conditions, the use of collector is very much increased.

The use of hydrochloric acid to lower the pH to 6.6, gives an unsatisfactory percentage recovery and assay value for the concentrate. Its use need not be further considered.

The depressant action of hydrofluoric acid on both sand and chrysocolla is contrary to what might be expected in consideration of results reported by Clemmer and Ambrose (9) on the separation of feldspar from quartz. They are able to depress the quartz in the mixture by hydrofluoric acid. Feldspar which is a silicate material, can then be separated at a pH of about 3. When the concentration of hydrofluoric acid is increased in these tests, so that the pH becomes about 3.5, copper of the chrysocolla goes into solution. This dissolving action decreases the amount of chrysocolla available for flotation; a condition, in itself, which results in an apparent depressant action.

Aluminum sulphate is of a type of compound that is reported by Eigeles, M. A. and Mokrousov, V. A. (23) to be a depressant for calcium carbonate, aluminum silicates (such as clays) and quartz. As mentioned before, aluminum sulphate also acts as a depressant for chrysocolla in the tests of this investigation.

CONCLUSION

The alkyl-substituted triphenyl methane dyes which for the purpose of this discussion are called butyl-malachite green, hexyl-malachite green, octyl-malachite green and octyl-rosaniline, all tend to promote the flotation of the mineral, chrysocolla. Octyl-malachite green shows better collecting properties than the others and has possibilities as a commercial flotation agent.

The flotation of chrysocolla from a quartz gangue can be accomplished with an enrichment of the concentrate of 850 percent as compared to the feed sample and a recovery of 64 percent. Higher recoveries or greater enrichment can be obtained but each is at the expense of the other.

Optimum conditions for flotation are not established. These conditions depend upon many factors. Most important of the factors seems to be the selection of efficient depressing agents for silica, dolomite, limestone and certain colloidal minerals such as clay. Other factors which are shown to be of major importance are: particle size of minerals in the pulp; rate of collector addition; length of the alkyl substituent in the dye; percentage of chrysocolla in the feed; and hydrogen ion concentration of the pulp. Trends with regard to these factors are shown but definite details are not determined.

Because of the lack of suitable depressants, the flotation of chrysocolla from impure dolomite and limestone is not accomplished. This problem as well as the details of the flotation of chrysocolla from silica may be worked out by further investigation.

The alkyl-substituted dyes are not a commercial product. Their present status of production is on the laboratory scale by which they are synthesized for this investigation.

APPENDIX

ORGANIC PREPARATIONS

GENERAL DISCUSSION

The alkyl-substituted dyes of the malachite green and rosaniline types are prepared for use as flotation agents. The chemical structure of intermediates and products is of much importance, but secondary to the flotation properties of the final product. For use as a flotation agent, a predetermined dye structure is desired, but a difference such as a branched chain is not important.

In the formation of the n-alkyl-phenyl-ketones by the Friedel-Crafts reaction, branching of the alkyl chain tends to take place (41). From the standpoint of flotation, this presence of side chains should increase collector efficiency. Swainson and Anderson (44) show that in the use of butyl-, amyl-, and hexyl-xanthates as collectors, the secondary compounds give the best recovery; the iso-compounds next; and the normal compounds the least recovery. Dean and Ambrose (12) point out that dissymmetry in the alkyl structure of amine collectors results in better flotation.

Similarly, the structure of the alkyl-rosaniline dye is unknown and may be a mixture such as is the commercial rosaniline dyestuff.

For the purpose of identification, these alkyl-substituted dyes are called: butyl-malachite green; hexyl-malachite green; octyl-malachite green; and octyl-rosaniline.

The first step in the synthesis is the preparation of the alkyl-benzenes, assumed to be normal alkyl-benzenes. They are used through a series of derivatives to obtain the final product.

For the malachite green dyes, a p-alkyl-benzaldehyde is formed and used as a reactant for the final dye. For the rosaniline dye, an o-octyl-aniline is formed and used in an ordinary rosaniline process.

The series of reactions for the preparation of each intermediate is indicated below:

Alkyl-benzene

$$C_6H_6 \xrightarrow[\text{Friedel-Crafts reaction}]{} C_6H_5.CO.R'$$

alkyl-phenyl-ketone

$$\xrightarrow[\text{Clemmensen reduction}]{} C_6H_5.R$$

alkyl-benzene

p-Alkyl-benzaldehyde

$C_6H_5 \cdot R \xrightarrow[\text{Friedel-Crafts reaction}]{} p\text{-}R \cdot C_6H_4 \cdot CO \cdot CO \cdot OC_2H_5$

ethyl-p-alkyl-phenyl-glyoxylate

$\xrightarrow{\qquad} p\text{-}R \cdot C_6H_4 \cdot CH \cdot N \cdot C_6H_5$

Schiff's base

$\xrightarrow{\qquad} p\text{-}R \cdot C_6H_4 \cdot CHO$

p-alkyl-benzaldehyde

o-Alkyl-aniline

$C_6H_5 \cdot R \xrightarrow[\text{nitration}]{} o\text{-}R \cdot C_6H_4 \cdot NO_2$

o-alkyl-nitrobenzene

$\xrightarrow[\text{reduction}]{} o\text{-}R \cdot C_6H_4 \cdot NH_2$

o-alkyl-aniline

In general, standard processes of reaction from the literature are used. Variations from this procedure must be made in many cases because of the high molecular weight of the compounds. Many of the compounds are of such high boiling point that decomposition results, even with low pressure distillation. Difficulties of preparation are found to increase with the length of the substituted hydrocarbon chain. The selection of the methods as outlined depends upon ease of preparation, yields to be expected, or in some cases upon arbitrary choice. A consideration of certain alternate methods is now made.

The formation of the alkyl-benzene is the first important step in the synthesis. The Wurtz-Fittig reaction, using bromo-benzene and an alkyl-halide was tried but rejected in favor of the method outlined. The alkyl-phenyl-ketone which is formed in the present synthesis may be reduced either by hydrogen in the presence of a catalyst or by the Clemmensen reduction. The Clemmensen reduction, giving a satisfactory product and being relatively convenient, is used.

Various methods for the preparation of aromatic ketones are outlined by Ferguson (25). Of these methods only relatively few can be applied to the alkyl-benzenes without destroying the alkyl-substituent. The method of Bouvealt (4) is found to be satisfactory because it places the aldehyde group in a position para to the alkyl chain. When a keto-carbonic acid is formed by using Bouvealt's method, it can be decomposed to the aldehyde by various paths. Hickinbottom (30) says that many α-keto-carbonic acids can be decomposed into the aldehyde or acid by merely warming with concentrated sulfuric acid. Bouvealt suggests forming an aryl-imino-derivative which can be decomposed into the aldehyde. The latter method is used by forming the Schiff's base.

An o-nitro-alkyl-benzene is required for the synthesis of the rosaniline dye. The p-nitro-compound, however, is formed in larger quantities by the direct nitration of the alkyl-benzene. An alternate method of blocking the para position and nitrating exclusively the ortho position, no doubt, would give increased yields. The extent of this apparent advantage might be lowered by an increase in the number of operations required. Only direct nitration of the alkyl-benzene is used.

Physical Data

Physical data on the alkyl-phenyl-ketones and on the alkyl-benzenes are readily available and to be considered accurate. Similar data on the derivatives of the alkyl-benzenes are to be used with caution. As an example, Rinkes (40) shows that physical data on the n-octyl-nitrobenzenes, as obtained by Ahrens (1) and included in Beilstein, are in error. Information in Beilstein on o-amino-n-octyl-benzene, which is derived from the octyl-nitrobenzene of Ahrens, is likewise to be doubted.

In this work, boiling points and sometimes indices of refraction of the main reaction products are designated in the procedure. Agreement with published values is not always obtained nor to be expected. A comparison of boiling points taken from the literature shows that they are frequently in poor agreement with each other. Boiling point data taken in this work also show that it alone cannot be used as a means of identification.

PREPARATION OF ALKYL-BENZENE

Alkyl-Acid-Chloride

The method for preparing alkylyl chlorides with thionyl chloride as described by Helferich and Schaefer (29) is used. The method is simple and proceeds smoothly. Yields on the lower homologues are relatively low, due partly to the small difference between the boiling points of the alkylyl chloride and thionyl chloride. The use of alternate methods with phosphorus trichloride, oxychloride or pentachloride could be expected to entail the same difficulty because of low boiling points.

The reaction as given by Weygand (51) is:

$$2\ RCOOH + SOCl_2 \longrightarrow 2\ RCOCl + SO_2 + H_2O$$

On the basis of this equation an excess of thionyl chloride must be used because water formed in the reaction causes hydrolysis of some thionyl chloride. The overall reaction is then:

$$RCOOH + SOCl_2 \longrightarrow 2\ RCOCl + SO_2 + HCl$$

Water or hydroxyl groups, including the carboxylic hydroxyl group, are attacked by thionyl chloride. In the overall reaction as carried out, 50 percent excess thionyl chloride is used.

Starting materials for the respective reactions are n-butyric acid, n-caproyl acid, and n-caprylic acid. Each is distilled for purification.

Procedure for Preparation of Alkylyl Chlorides

Reactants

1.5 mol	thionyl chloride
1.0 mol	n-alkyl acid

The thionyl chloride is placed in a 2-necked, round bottom flask provided with a reflux condenser and dropping funnel. It is brought to a boil and the n-alkyl acid is added dropwise at such a rate as to regulate the evolution of hydrochloric acid gas. After the alkyl acid has been added, the solution is boiled for two hours and allowed to stand over night. The excess thionyl chloride is distilled off (78.8°C.) and the alkyl acid-chloride is fractionated.

Alkyl Acid-Chloride	B.P.	Yield %
n-caprylyl chloride	163-165°C.(15 mm.)	80
n-caproyl chloride	147-151°C.(740 mm.)	50-59
n-butyryl chloride	98-101°C.(1 atm.)	57

Alkyl Phenyl Ketone

The formation of the ketone from the n-alkylyl chloride and benzene is carried out by a Friedel-Crafts reaction in a method similar to that described by Ju, Shen, and Wood (32) except that carbon disulfide is not used as a diluent. The presence of carbon disulfide is said to regulate the reaction by forming a complex with aluminum chloride, but good results are obtained without its use. An excess of benzene as a diluent, as used, presents less difficulties in purification. The presence of even small amounts of carbon disulfide gives poor results in the succeeding Clemmensen reduction.

The overall reaction may be represented by the equation:

$$C_6H_6 + RCOCl \xrightarrow[AlCl_3]{} C_6H_5.CO.R + HCl$$

The mechanism of the process includes the formation of an aluminum chloride complex which as noted by Shen, Ju, and Wood, allows the formation of branched chain alkyl groups in the ketone. These isomers, if present in the product would constitute an impurity but would not interfere with the ultimate utility of succeeding products.

Both boiling points and indices of refraction are used for identification of the products. Ju, Shen, and Wood give values of refractive indices for a series of n-alkyl-phenyl-ketones over a range of temperature.

The values for the ketones prepared in this work are not included in their results, but by interpolation, a quite accurate estimate can be made.

Three normal alkyl-phenyl-ketones are prepared, namely: n-propyl-phenyl-ketone; n-amyl-phenyl-ketone; and n-heptyl-phenyl-ketone.

Procedure for Preparation of Alkyl-phenyl Ketone

Reactants

.77 mols	alkyl-acid-chloride
2.12 mols	anhydrous aluminum chloride
21.2 mols	benzene

The dried benzene is placed in a 5-liter, 3-necked, round bottom flask provided with a mercury sealed stirrer, a reflux condenser and a dropping funnel. The flask is cooled with a salt-cracked-ice bath. The aluminum chloride is added and the mixture is cooled to 10°C., at which temperature it is maintained during the reaction. The alkyl-acid-chloride is addedfrom a dropping funnel over a period of two hours. The progress of the reaction can be followed by the evolution of hydrochloric acid. To start the reaction a slightly higher temperature may be used.

The reaction mixture is maintained at 10°C. for five hours after the addition of the acid chloride. It is then packed with ice and allowed to stand over night. The mixture is again cooled and poured on cracked ice which has been acidified with hydrochloric acid. It is allowed to stand for two hours without stirring. Benzene is distilled off and the ketone is washed twice with boiling sodium carbonate solution and then with water. The ketone is dried and fractionated.

Alkyl-phenyl-ketone	B.P.°C.	Index of Refraction	% Yield
n-heptyl-	163-164 (15 mm.)	1.5050 (21°)	90
n-amyl-	132-136 (15 mm.)	1.5106 (22°)	82
n-propyl-	108-110 (15 mm.)	1.5172 (25°)	73

Ketone Reduction

The reduction of the ketone to the hydrocarbon is carried out by means of the Clemmensen reduction with amalgamated zinc and hydrochloric acid. The method as described by Martin (33) and carried out by Johnson and Kohmann (31) is used.

By using a large volume of amalgamated zinc to increase the area of contact with the reacting solution, little difficulty is encountered in the reduction. The condition of the zinc surface is an essential factor.

It is found that by reconditioning the used amalgamated zinc, through heating with dilute hydrochloric acid, a satisfactory surface can be restored. The best yields of n-alkyl-benzene are obtained with reconditioned or continually used zinc. Reconditioning of the zinc represents a considerable saving in the cost of zinc because of the large quantities that are used.

Depending upon the zinc surface, yields of alkylbenzene vary from 20 to 70 percent.

Both mossy zinc and zinc-foil rolled into spirals proved effective to about the same degree.

The reaction is represented by the formula:

$$C_6H_5{\cdot}CO{\cdot}R' + 4\ (H) \longrightarrow C_6H_5{\cdot}CH_2{\cdot}R' + H_2O$$

When the surface of the amalgamated zinc is in poor condition, excessively large amounts of a heavy oily substance form. Yields may be decreased to a negligible amount. Even under the best operating conditions, a relatively large amount of the heavy oil is formed.

Procedure for Preparation of Mossy Zinc

Reactants

1668	gm.	mossy zinc
117	gm.	mercuric chloride
83	cc.	conc. hydrochloric acid
1500	cc.	water

The mercuric chloride is dissolved in water to which a small amount of hydrochloric acid is added. The zinc is placed in a 2-liter Erlenmeyer flask. The acidified mercuric chloride solution is added to the zinc, shaken for five minutes and poured off. It is then used immediately.

An old zinc surface can be regenerated by heating with a dilute hydrochloric acid solution for a couple of hours.

Procedure for Preparation of Alkyl-phenyl-Ketone

Reactants

200 gm.	alkyl-phenyl-ketone
750 gm.	conc. hydrochloric acid
750 gm.	xylene

The amalgamated zinc is covered to half its height with concentrated hydrochloric acid. The ketone and the xylene are then added. The flask is provided with a reflux condenser and a source of gaseous hydrochloric acid to replace that used. Under these conditions, it is refluxed for seven hours.

The reaction mixture is poured from the flask and separated. The xylene layer is washed several times with water. The xylene is evaporated off and the alkyl benzene fractionated.

For purification, the alkyl benzene is heated for several hours at 160°C. with sodium metal and then distilled in the presence of molten sodium.

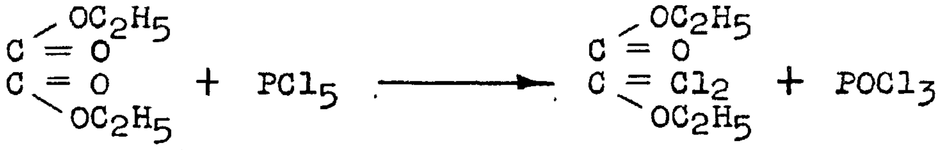
Alkyl Benzene	B.P.°C.	Refract.Index	% Yield
Octyl-benzene	133-139 (15 mm.)	1.4858 (25°)	30-70
Hexyl-benzene	98-99 (15 mm.)	1.4869 (27°)	69
Butyl-benzene	70-74 (15 mm.)	1.4930 (24°)	70

PREPARATION OF ALKYL-SUBSTITUTED MALACHITE GREEN DYES

Ethyl-oxalyl-chloride

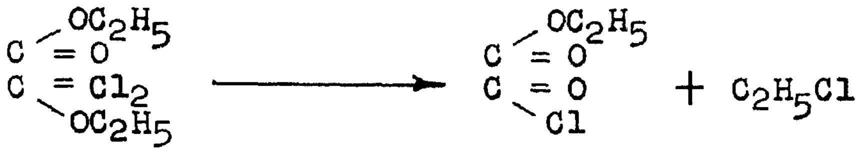
Ethyl-oxalyl-chloride is to be used for the preparation of alkyl-benzaldehydes by the method of Bouveault (4). Preparation of ethyl-oxalyl-chloride is carried out according to the method of Weygand (53) with suggestions from Anschutz (2).

Upon heating diethyl-oxalate with phosphorus pentachloride at about 125°C., an intermediate, ethyl-dichloro-oxyacetate forms as shown:



If heated to over 130°C., the ethyl-dichloroxyacetate decomposes into oxalyl-chloride but because of small differences in boiling points is difficult to separate from phosphorus oxychloride. A distillation under vacuum, however, removes the phosphorus oxychloride without decomposition of the other material. The ethyl-dichloroxyacetate can then be decomposed and separated with relatively little difficulty.

Upon heating ethyl-dichloroxyacetate to about 135°C., the decomposition takes place quite slowly. Weygand (53) suggests using a platinum catalyst to speed the decomposition. Without the catalyst the reaction does take place slowly but with satisfactory results. The decomposition is represented by the equation:



Ethyl-dichlor-
oxyacetate

Ethyl-oxalyl-
chloride

Ethyl chloride is evolved as a gas.

The boiling point of ethyl-oxalyl-chloride is given by Weygand (53) as 130.5 to 132°C., by Anschutz (2) as 134-135°C.

Procedure for Preparation of Ethyl-oxalyl-chloride

Reactants

1.0 mol	phosphorus pentachloride
.71 mol	di-ethyl oxalate

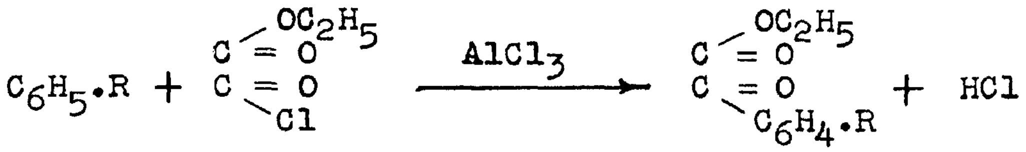
The reactants are placed in a round-bottom flask equipped with a reflux condenser and heated at not over 130°C. for 15 hours. The material is then fractionated at 40 mm. Vacuum is necessary in order to prevent decomposition of the ethyl-dichloro-ethoxyacetate. The lower boiling fraction contains phosphorus oxychloride and the higher boiling fraction, the ethyl-dichloro-ethoxyacetate (96°C. at 40 mm.). The ethyl-dichloro-ethoxyacetate is placed in a flask provided with a short unpacked column and a distillation head. Upon heating to about 135°C. under reflux, some of the ethyl-dichloro-ethoxyacetate is decomposed into ethyl-oxalyl-chloride with the evolution of gas. The ethyl-oxalyl-chloride formed is then distilled off at 136°C. and heating under reflux is repeated. By merely increasing and decreasing the temperature on the flask in one-half hour cycles, the process is continued until oxalyl-chloride no longer seems to form. The crude ethyl-oxalyl-chloride is then fractionated.

Ethyl-oxalyl-chloride	B.P. 129-134°C.	Yield 75% (approx.)

Alkyl-Benzaldehyde

Bouveault's method (4) for forming the aldehyde is used. The procedure as outlined by Weygand (55), in general, is followed. The alkyl-benzene when subjected to a Friedel-Crafts reaction with ethyl-oxalyl-chloride forms an ethyl-p-alkyl-phenyl-glyoxylate. This places the substituent in the desired para position. Carbon disulfide and nitrobenzene as solvents are used in the Friedel-Crafts reacting mixture. Thomas (47) mentions that better results are obtained with compounds of high reactivity when a complex is formed, as with nitrobenzene.

The Friedel-Crafts reaction is represented by the following equation:



Ethyl-oxalyl-chloride

Ethyl-p-phenyl-glyoxylate

The ethyl-p-alkyl-phenyl-glyoxylate is distilled at 10 mm. pressure for purification. Even under vacuum some decomposition occurs. After distillation, the product is saponified with caustic and acidified with dilute hydrochloric acid. The steps are represented in the following scheme:

$$p\text{-}R.C_6H_4.CO.CO.OC_2H_5 \xrightarrow[NaOH]{} p\text{-}R.C_6H_4.CO.CO.ONa$$

Ethyl-p-alkyl-phenyl glyoxylate

Sodium-p-alkyl-phenyl glyoxylate

$$\xrightarrow[HCl]{} p\text{-}R.C_6H_4.CO.COOH$$

p-Alkyl-phenyl-glyoxylic acid

The p-alkyl-phenyl-glyoxylic acid can be used as a crude product from an ether extract. This is advisable because considerable loss may occur from purification. Distillation of the higher glyoxylic acids at 8 mm. pressure is found to result in serious loss by decomposition. The crude p-alkyl-phenyl-glyoxylic acid when treated with freshly distilled aniline forms the Schiff's base. Purification of the Schiff's base by distillation gives serious decomposition with both compounds above the butyl derivative. Formation of the Schiff's base and its decomposition into the aldehyde are represnted below:

$$p\text{-}R.C_6H_4.CO.COOH \xrightarrow[C_6H_5.NH_2]{} p\text{-}R.C_6H_4.CH.N.C_6H_5$$

Schiff's base

$$\xrightarrow[\text{dilute } H_2SO_4]{\text{heat}} p\text{-}R.C_6H_4.CHO$$

p-Alkyl-benzaldehyde

The intermediates prepared are the p-butyl-, p-hexyl-, and p-octyl-benzaldehydes.

Procedure for Preparation of p-Alkyl-benzaldehyde

Reactants

.405	mol	alkyl benzene
73.	gm.	nitrobenzene
184.	gm.	carbon disulfide
.52	mol	anhydrous $AlCl_3$
.486	mol	ethyl-oxalyl-chloride

All materials except the oxalyl-chloride are put into a 500 cc. flask provided with a mercury sealed stirrer, a reflux condenser, and a dropping funnel. The ethyl-oxalyl-chloride is added from a dropping funnel so as to regulate the rate of reaction. When the evolution of hydrochloric acid gas has ceased, the mixture is poured on cracked ice to which hydrochloric acid has been added. The nitrobenzene is used to control the rate and allow complete reaction of the aluminum chloride.

The oily material is extracted with ether, separated, washed twice with dilute sodium carbonate solution and twice with water. The carbonate wash is saved because it contains a considerable amount of the sodium salt of glyoxylic acid. The wash is acidified, extracted with ether and later combined with the main portion of glyoxylic acid.

The washed material is dried and the ether and carbon disulfide are distilled off. The glyoxylate dissolved in nitrobenzene is separated by simple distillation.

Substituted phenylglyoxylate	B.P.°C.	Index of Refraction	% Yield
Ethyl-p-n-octyl-	214-230 (8 mm.)	1.501 (30)	59
Ethyl-p-n-hexyl-	200-214 (10 mm.)		65
Ethyl-p-n-butyl-	160-180 (10 mm.)	1.515 (28)	59

The distillate is boiled with 20 gm. (.5 mol) sodium hydroxide until a homogeneous solution is formed, is acidified with hydrochloric acid, and is extracted with ether. Free acid from the sodium carbonate wash is combined with this solution and it is dried over anhydrous sodium sulfate. The ether is vaporized and the crude acid is used in the following reactions to form the Schiff's base.

An excess of freshly distilled aniline, 30 gm. (.325 mol) is mixed with the crude acid in a Claisen flask. Upon heating, an evolution of gas takes place forming the Schiff's base. Distillation of the Schiff's base even under reduced pressure, causes considerable decomposition, especially of the higher compounds. Only the butyl-compound is distilled.

Schiff's Base	B.P.°C.	% Yield
Butyl compound	185-199 (9 mm.)	20

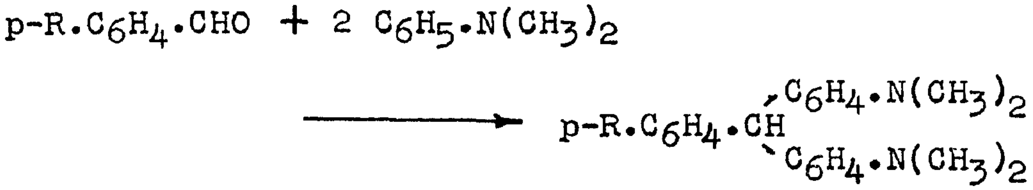
If the Schiff's base is not distilled, aniline and water are removed under vacuum and the impure Schiff's base is hydrolyzed with 310 cc. of 25 percent sulfuric acid. The aldehyde is then extracted with ether, dried over anhydrous sodium sulfate and distilled.

p-Alkyl-benzaldehyde	B.P.°C.	Mols	% Yield
p-Octyl-	175-190 (10 mm.)	.127	32
p-Hexyl-	155-159 (10 mm.)	.081	30.6
p-Butyl-	115-140 (11 mm.)	.039	9.6

Overall yields as given are based on the amount of alkyl-benzene as starting material.

Alkyl-Malachite Green Dye

The leuco-base is first formed and it is then oxidized to the dye with lead dioxide. The formation of the leuco-base is carried out according to the procedure of Cain and Thorpe (5). The p-alkyl-benzaldehyde is reacted with dimethyl-aniline to form the leuco-base as shown.



$$p\text{-}R\cdot C_6H_4\cdot CHO + 2\ C_6H_5\cdot N(CH_3)_2 \longrightarrow p\text{-}R\cdot C_6H_4\cdot CH\begin{matrix}\diagup C_6H_4\cdot N(CH_3)_2\\ \diagdown C_6H_4\cdot N(CH_3)_2\end{matrix}$$

Leuco-base

For the oxidation of the leuco base, better results are obtained by using a method outlined by Weygand (54). The recovery of dye is more difficult as the alkyl-chain length increases. This is due to a decrease in solubility. When filtering the oxidized dye from the lead peroxide precipitate, it is essential that the precipitate be washed free of dye.

Procedure for Preparation of Alkyl-substituted Dyes

Reactants

.1 mol	alkyl benzaldehyde
22. gm.	dimethyl aniline
25.5 gm.	concentrated hydrochloric acid

The reactants are placed in a small round-bottom flask equipped with an air cooled reflux condenser and heated at 100°C. for 24 hours. After refluxing, the mix is made alkaline and steam distilled to remove the unreacted material. Long chain alkyl benzaldehydes are relatively difficult to vaporize, but since they can be removed in a later operation, their complete removal is not necessary. After the steam distillation, the reaction products are poured into about 600 cc. of water. A thick oily material separates, which may be removed in a separatory funnel or on a filter paper. This leuco-base is of honey like color and consistency.

Malachite Green Dye	Mols	% Yield
Octyl-leuco-base	.09	90 (est.)
Hexyl-leuco-base	.09	90
Butyl-leuco-base	.09	90

The leuco-base contains some impurities which are removed in a later purification.

Procedure for Oxidation of the Leuco-base

Reactants

.09	mols	Alkyl-leuco-base
363.	cc.	hot normal hydrochloric acid
21.6	gm.	lead peroxide
182.	cc.	water

The leuco-base is dissolved in the hot normal hydrochloric acid, diluted to about a liter and allowed to cool. The lead peroxide is suspended in the water and then added over a period of five minutes to the solution containing the leuco-base, with constant shaking. It is then heated at about 100°C. for another five minutes. The solid material is filtered with suction from the solution. The material on the filter is washed with ethanol in order to recover the undissolved dye. The wash is combined with the filtrate. Some sodium sulphate is added to the filtrate to precipitate dissolved lead and it is filtered again. The filtrate is now made basic with caustic solution in order to precipitate the color-base. This color-base is allowed to dry on the filter for a short time and is then removed and dissolved in benzene. Dry hydrochloric acid gas is passed through the benzene solution until the dye is completely precipitated as a solid or a thick tarry like substance. The benzene is decanted off, the solid allowed to drain and dry, and the product is recovered.

Alkyl-malachite Green	% Yield (basis, aldehyde)	% Yield (alkyl-benzene)
Octyl-	15	4.8
Hexyl-	50	15.3
Butyl-	51	5.0

In all cases the product is a green dye and a solid. With greater alkyl chain length the dye becomes less soluble.

PREPARATION OF ALKYL-SUBSTITUTED ROSANILINE DYES

Nitration of the Alkyl-Benzenes

The usual methods of nitration can not be used to substitute the nitro-group on the aryl-ring of the alkyl-benzenes because of the relative reactivity of the hydrocarbon chain. Rinkes (40), however, shows that by using fuming nitric acid at -5°C. good yields are obtained. Of the total yield he obtains about 27 percent of ortho-nitrobenzene, the rest being mainly para-nitrobenzene. For the preparation of the alkyl-rosaniline, only the ortho-substituted compound is used.

Rinkes also shows that previous work on the octyl-nitrobenzene by Ahrens (1) is in error. Physical data on the compounds in Beilstein are likewise in error. Rinkes gives 182-184°C. (10 mm.) for the boiling point of o-octyl-nitrobenzene.

Both the hexyl-nitrobenzene and octyl-nitrobenzene are prepared.

Procedure for Preparation of o-Alkyl-nitrobenzene

Reactants

.615	mol	n-alkyl-benzene
150.	cc.	fuming nitric acid (sp. gr. 150)

The alkyl-benzene is placed in a 500 cc. 3-necked flask provided with a dropping funnel, a mechanical stirrer and a reflux condenser. The flask is cooled and maintained at -5°C., while the fuming nitric acid is added drop by drop from the dropping funnel. The addition of the acid requires between four and five hours.

The reaction product is poured on ice, diluted with benzene and separated from the acid solution. Dilution with benzene allows the oily layer to float on the water. The product is washed with water, with soda ash solution and again with water.

After distilling off the benzene, the combined ortho- and para-nitro-octyl-benzene mixture is subjected to fractionation under vacuum. The ortho-nitro fraction is redistilled under vacuum.

o-Nitro-n-alkyl-benzene	B.P.°C.	Index of Refraction	% Yield
Octyl-	174-179 (10 mm.)	1.507 (29°)	29
Hexyl-	155-162 (10 mm.)	1.515 (29°)	20

Reduction of Ortho-nitro-alkyl-benzene

Weygand (56) states that the tendency toward side reactions is especially prevalent during the reduction of aromatic nitro-compounds when stannous chloride or zinc is used with hydrochloric acid. The use of iron as outlined by West (50) suppresses this tendency toward chlorine substituted products. The method of West has been followed.

Procedure for Reduction of o-Nitro-alkyl-benzene

Reactants

.2	mol	o-nitro-n-alkyl-benzene
100.	cc.	methanol
3.5	cc.	concentrated hydrochloric acid
33.	gm.	iron filings

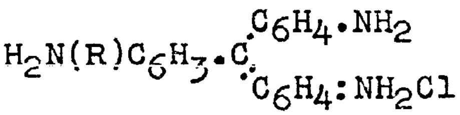
The nitro-compound, the methanol, and the hydrochloric acid are placed in a 250 cc., 3-necked flask equipped with a heater, mechanical stirrer and reflux condenser. The material in the flask is brought to a boil and the iron filings are added in four portions over five minutes. It is then refluxed for two hours. Since the amine formed has very low volitility, steam distillation is not used for its removal from the reaction mixture. The hydrochloric acid is neutralized by a calculated amount of sodium hydroxide (2.58 gm.) in solution. The residue is filtered off and the methanol is vaporized. A small excess of hydrochloric acid is added and the material is cooled to 20°C. A thick pasty mass separates which can be filtered cold, or with the amines of lower molecular weight, a liquid separation can be made. The volume of aqueous solution should be kept very small before the separation because the hydrochloride is quite soluble. The alkyl-aniline-hydrochloride is treated with caustic, absorbed in ether, and dried over anhydrous sodium sulphate and distilled.

Alkyl-aniline	B.P.°C.	% Yield
o-Octyl-aniline	172-177 (13 mm.)	85
o-Hexyl-aniline	151-166 (13 mm.)	80

The percent yield is given on the basis of the nitro-compound.

Octyl-rosaniline Dye

The method outlined for the preparation of rosaniline by Cain and Thorpe (6) is used for the preparation of octyl-rosaniline. Ortho-octyl-aniline is substituted for o-toluidine. The method is known to produce a variety of products. It can be expected to do so in the preparation of octyl-rosaniline. The structural formula of this product is not definitely known but from the procedure followed is assumed to be:



$$H_2N(R)C_6H_3\cdot C\begin{matrix}\cdot C_6H_4\cdot NH_2\\ \cdot C_6H_4{:}NH_2Cl\end{matrix}$$

Octyl-rosaniline

The method proceeds according to the method of Cain and Thorpe to the point of salting out the dye. Here, in place of crystals forming, an oily material forms on the surface. It contains many impurities which must be separated in order to obtain the purified octyl-rosaniline.

During the purification, a number of other compounds are noticed by their color. A brown oil-soluble substance is separated. A black substance which is relatively insoluble in dilute alcohol is also separated. The latter substance gives a violet to brown color in strong alcohol solution.

The percentage yield of octyl-rosaniline is based on the octyl-aniline used in the reaction mixture. The very low yield reported is due to three main factors. The octyl-aniline is used 24 percent in excess in the reaction mixture; side-reactions are prevalent; and some of the material is lost in attempting different methods of separation. The yield to be expected on making ordinary rosaniline is only about 40 percent.

Procedure for Preparation of Octyl-rosaniline

Reactants

6.2 gm.	aniline
7.1 gm.	p-toluidine
19.0 gm.	conc. hydrochloric acid
17.0 gm.	o-octyl-aniline

These reactants are heated to 130°C. in a 3-necked 500 cc. flask. Then the rest of the reactants are added.

3.1 gm.	aniline
3.6 gm.	p-toluidine
12.9 gm.	o-octyl-aniline
20.4 gm.	nitrobenzene

The flask is now provided with a mechanical stirrer and a thermometer, and is heated to 100°C.

Iron powder, 1.1 gm., dissolved in hydrochloric acid is added over a period of a few minutes.

Leaving one of the flask openings open for the vaporization of water, the flask is gradually heated to about 180°C. At a temperature below 180°C. an air cooled reflux condenser is connected to the remaining flask opening. Heating at 180°C. is continued for about 4 hours.

During the heating period, a red color develops in the reaction mixture. When material from the reaction mixture becomes solid on a glass rod, the reaction is considered complete.

Aniline and toluidine may be steam distilled from the reaction mixture but unreacted octyl-aniline distils with difficulty. Complete separation is not made.

After steam distillation, the melt is poured with stirring into 200 cc. of boiling water. 4.5 cc. of concentrated hydrochloric acid are added to obtain an acid reaction and the mixture is boiled for a few minutes. Care must be exercised during boiling because of the tendency to foam.

The dye is salted out with about 10 grams of salt. A black oily layer and a black aqueous layer form on standing. They can be separated by use of a separatory funnel by noting the difference in viscosity. After separation the oily layer is again treated with water and acid and again salted out. The aqueous layer contains much less black material and is easier to separate. After the second separation of the oily layer, it is placed in a beaker and heated to about 60°C. A black tarry substance separates and is removed. Beakers and the separatory funnel used become coated with the black tarry material. It is dissolved off with alcohol and after vaporization of the alcohol is returned to the main body of material. Dissolved in alcohol, the material has a red color.

The tarry mass is treated with a small amount of hot water, and after drying, with benzene. A black tarry material remains which turns to a hard resinous substance on standing.

The solid substance is extracted with a 50 percent alcohol solution until the color of the alcohol begins to change from a red to a purplish red color. The extract is evaporated down until a brown solution is left. The tarry substance which separates out is washed with water and taken as the product.

		% Yield, basis of:	
	Grams	octyl-aniline	octyl-benzene
Octyl-rosaniline	7.8	15	3.7

The product is a dye of red color. It has very little solubility in water or in benzene, but is soluble in concentrated ethanol.

DATA

FLOTATION OF CHRYSOCOLLA

Collector: butyl-malachite green

Mineral mixture: 1 gm. chrysocolla, 99 gm. sand,
.235 % copper

Frother: pine oil as needed

						Concentrate		
Exp. No.	Mesh	Agent	#/ton	Min.	pH	Grams	cc.N/10 $Na_2S_2O_3$	Date 1947
15	150-200	HF	.03	7	4.3	2.34	nil	3-26
16	150-200	HF	.024	8	4.1		trace	3-26
32-A	-200		.01	2	8.3	2.23	2.6	4-4
-B			.01	2		1.55	1.6	
-C			.01	2		1.84	1.2	
-D			.01	2		1.23	1.0	
-E			.01	2		1.70	1.0	

Mineral mixture: 1 gm. chrysocolla, 99 gm. dolomite
.235 % copper

						Concentrate		
Exp. No.	Mesh	Agent	Dye #/ton	Time Min	pH	Grams	cc.N/10 $Na_2S_2O_3$	Date 1947
12	-200	no pine oil	.054	3	7.8	3.52	trace	3-25
13	-200		.036	2	7.9	7.05	some copper	3-25

Exp. No.	Mesh	Agent	Dye #/ton	Time Min.	pH	Concentrate		Date 1947
						Grams	cc. N/10 $Na_2S_2O_3$	
33-A	-200	$Al_2(SO_4)_3$ .4 #/ton	.01	2	7.9	2.08	trace	4-4
-B			.01	2		1.66	trace	
-C			.01	2		1.79	nil	
-D			.01	2		1.02	trace	
-E			.01	2		1.22	trace	
-F			.01	2		1.50	trace	
-G			.01	2		1.47	trace	
-H			.01	2		.89	nil	

A large amount of aluminum hydroxide is formed in the chemical analysis.

Collector: hexyl-malachite green

Mineral mixture: 1 gm. chrysocolla, 99 gm. sand,
.235 % copper

Frother: pine oil as needed

Exp. No.	Mesh	Agent	Dye #/ton	Time Min.	pH	Concentrate		Date 1947
						Grams	cc. N/10 $Na_2S_2O_3$	
4	150-200		.028	2	7.8	1.40	1.4	3-22
5	-200		.03	3	7.8	2.49	4.2	3-22
10	-200	HCl	.03		2.3	12.24	nil	
28-A	-200	HF	.02	2	4.1	3.49	.1	4-1
-B			.01	1		6.61	3.0	

Exp. No.	Mesh	Agent	Dye #/ton	Time Min.	pH	Concentrate Grams	Concentrate cc.N/10 $Na_2S_2O_3$	Date 1947
30-A	-200	HF	.01	2	4.0	1.52	.2	4-1
-B			.01	2		3.79	1.6	
-C			.01	2		4.30	1.0	
37	-200	H_2SO_4	.11	4	4.7	12.71	.9	
31-A	-200		.01	2	7.9	2.50	3.9	4-2
-B			.01	2		2.48	4.6	
-C			.01	2		4.52	6.7	
-D			.01	2		5.94	3.1	
-E			.01	2		7.40	3.6	
-F			.01	2		5.90	.6	
-G			.02	2		10.90	trace	

Mineral mixture: 2 gm. chrysocolla, 98 gm. sand,

.47 % copper

Exp. No.	Mesh	Agent	Dye #/ton	Time Min.	pH	Concentrate Grams	Concentrate cc.N/10 $Na_2S_2O_3$	Date 1947
A-11	150-200	HF			3.4	2.20	1.4	3-13
27	-200	HF	.05	2	4.1	4.61	5.5	3-28
A-17	-200	HF, citric acid .5 #/ton	.016	6	3.6	2.08	2.0	3-17
A-13	-200	HCl .4 #/ton	.01	5	4.0	1.75	3.2	3-17
-B			.01	5		3.33	4.6	

Mineral mixture: 1 gm. chrysocolla, 99 gm. dolomite,

.235 % copper

						Concentrate		
Exp. No.	Mesh	Agent	Dye #/ton	Time Min.	pH	Grams	cc.N/10 $Na_2S_2O_3$	Date 1947
A-4	-150 (not deslimed)		.02	7	7.2	30.2		2-25
6	150-200		.03	3	7.4	5.16	nil	3-22
1	-200	Na_3PO_4 .5 #/ton	.014	6	8.2	4.51	1.0	
2	-200	$Al_2(SO_4)_3$ .32 #/ton	.014		7.0	5.76	2.5	
3	-200	sodium silicate .4 #/ton	.014				nil	
9	-200	acetic acid 14.7 #/ton	.04	5	7.1	8.47	nil	3-24
8-A	-200	acetic acid 4.2 #/ton	.04	3	7.4	11.97	nil	3-24
-B			.022			7.64	nil	

Mineral mixture: 2 gm. chrysocolla, 98 gm. dolomite,

.47 % copper

						Concentrate		
Exp. No.	Mesh	Agent	Dye #/ton	Time Min.	pH	Grams	cc.N/10 $Na_2S_2O_3$	Date 1947
25-A	-200		.06	1		9.58	3.3	3-28
-B			.06	1.5		4.75	2.5	

Collector: octyl-malachite green

Mineral mixture: 1 gm. chrysocolla, 99 gm. sand,
.235 % copper

Frother: pine oil as needed

						Concentrate		
Exp. No.	Mesh	Agent	Dye #/ton	Time Min.	pH	Grams	cc.N/10 $Na_2S_2O_3$	Date 1947
34-A	-200		.01	2	8.0	1.19	2.4	4-5
-B			.01	2		2.05	4.5	
-C			.01	2		1.44	3.6	
-D			.01	2		1.52	3.5	
-E			.01	2		1.60	3.9	
-F			.01	2		.75	1.7	
36-A	-200		.03	2	8.1	1.82	6.5	4-8
-B			.03	2		1.56	6.5	
-C			.03	3		1.94	6.5	
-D			.03	3		2.20	4.4	
-E			.02	2		2.54	3.7	
-F			.03	2		1.53	.9	
-G			.024	2		3.37	.8	
43-A	-200	conc.HCl .01 cc.	.03	2	6.6	2.02	3.8	4-12
-B			.03	3		2.09	3.4	
-C			.03	2.5		1.83	3.6	
-D			.03	2.5		3.42	3.3	
-E			.03	2.5		3.07	3.1	
-F			.03	2.5		2.43	2.2	

Exp. No.	Mesh	Agent	Dye #/ton	Time Min.	pH	Concentrate Grams	cc.N/10 $Na_2S_2O_3$	1947
37	-200	H_2SO_4	.11	9	4.7	12.71	.9	4-9
47-A	-200	Na_2CO_3 .04 gm.	.04	3	8.1	.58	2.2	4-16
-B			.04	3		.44	2.7	
-C			.04	3		.85	4.1	
-D			.04	3		2.48	7.6	
-E			.04	3		3.12	4.7	
-F			.04	3		3.53	4.4	

Mineral mixture: 1 gm. chrysocolla, 99 gm. dolomite,

.235 % copper

Exp. No.	Mesh	Agent	Dye #/ton	Time Min.	pH	Concentrate Grams	cc.N/10 $Na_2S_2O_3$	Date 1947
40-A	-200	$Al_2(SO_4)_3$ .4 #/ton	.04	2	8.0	5.79	1.5	4-11
-B			.04	3		1.66	nil	
-C			.04	2		1.11	nil	
-D			.04	2		.63	nil	
-E			.12	7		9.07	nil	

Collector: octyl-rosaniline

Mineral mixture: 1 gm. chrysocolla, 99 gm. sand,
.235 % copper

Frother: pine oil as needed

Exp. No.	Mesh	Agent	Dye #/ton	Time Min.	pH	Concentrate		Date 1947
						Grams	cc.N/10 $Na_2S_2O_3$	
38-A	-200		.04	2	8.0	5.34	5.0	4-10
-B			.04	2		7.19	1.8	
39-A	-200		.02	2	8.3	1.82	2.8	4-11
-B			.02	2		2.68	2.5	
-C			.01	2		2.73	1.5	

Mineral mixture: 1 gm. chrysocolla, 99 gm. dolomite
.235 % copper

Exp. No.	Mesh	Agent	Dye #/ton	Time Min.	pH	Concentrate		Date 1947
						Grams	cc.N/10 $Na_2S_2O_3$	
42-A	-200	$Al_2(SO_4)_3$ .38#/ton	.03	2		2.52	1.0	4-12
-B			.03	2		.67	nil	
-C			.03	2		.52	nil	
-D			.06	4		1.98	1.5	
-E			.04	4		.50	.5	

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