

FLOTATION OF TITANIUM ORE BY 2-NITRO-4-ALKYL PHENOLS

Thesis for the Dogree of M. S. MICHIGAN STATE COLLEGE Kalyanji U. Patel 1953 This is to certify that the

thesis entitled

FLOTATION OF TITANIUM ORE BY 2-NITRO-L-ALKYL PHENOLS

presented by

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has been accepted towards fulfillment of the requirements for

MASTER OF SCIENCE degree in CHEMICAL ENGINEERING

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Major professor

Date May 26, 1953

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2- NITRO - 4 - ALKYL PHENOLS.

BY

KALYANJI U. PATEL.

A THESIS

Submitted to the School of Graduate Studies of Michigan State College of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of

M.S.

Department of Chemical Engineering Year 1953



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ACKNOWLEDGMENTS

The author wishes to express his appreciation to Dr. Clyde C. DeWitt for the guidance and encouragement in the pursuance of this research project.

The author also wishes to extend his appreciation to Dr. Harold A. Price and I. A. Patel for the valuable guidance in the synthesis of the collectors.

CONTENTS

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I.	INTRODUCTION
	Purpose and Scope
	Previous work in the Titanium Flotation 4
	Theory
II.	DESIGN OF THE COLLECTOR
III.	EXPERIMENTAL PART
	Flotation machine
	Addition of the reagents
	Quantitative determination of the Titanium 18
IV.	DATA AND RESULTS
	Tables 2-6
	Graphs, Figures 4-6
	Discussion of the results
	Conclusions
	APPENDIX
	Synthesis of 2 Nitro 4 Alkyl Phenol 35
	BIBLIOGRAPHY

INTRODUCTION

Titanium generally occurs in nature as an titanium dioxides mixed with the oxides of the other elements. Common titanium ores are: Rutile, Ilmenite, Apatite, Brookite, Anatase, Arizonite, Titanite, Perovskite. Titanium is the ninth in abundance of the elements of the lithosphere; it accounts for 0.62% of the total lithosphere. Titanium is five to ten times more abundant than such well known non-metals as sulphur and phosphorous; the commercially important titanium minerals are Ilmenite, rutile and Apatite.

Sands of the seashore generally contain titanium dioxides in very small amounts. In the United States high grade titanium ores are found in Virginia, North Carolina, New York, Colorado, California and Florida. In India these ores are found in Travancore and Mysore. Other potentially important deposits occur in Norway, Canada, Africa, Latin America, Brazil and Argentina.

William Haynes first recognized the difference in the wettability of the minerals by water. He used this property in the flotation as described in his British Patent No. 488 granted in 1860.¹² In the succeeding fifty years, flotation practice passed through many phases of development, such as bulk oil flotation, skin flotation, and froth flotation. The historical sketch of this development is given in table No. 1.

(1)

Table No. 1.

Important Steps In The Evolution of Flotation (13)

Approxi- mate Date	Name of Inventor	Invention
1860	Ha ynes	Usefulness of differences in wettability of minerals by water and oil.
1886	Everson	Use of acidulated pulps.
1902	Froment; potter, and Delprat	Use of gas as a buoyant medium.
1905	Schwarz	Use of sodium sulphide to re- cover oxidized base metal minerals.
1906	Sulman, Picard, and Ballot	Reduced amount of oil; intro- duction of gas by violent agitation.
1 90 9	Greenway, Sulman, and Higgins	Soluble frothing agent.
1913	Bradford	Copper sulfate as an activa- tor for sphalerite.
1913	Bradford	Sulfur dioxide to depress sphalerite.
1921	Perkins	Specific organic collectors.
1921	Perkins	Alkaline circuits.
1922	Sheridan and Griswold	Cyanides to depress sphalerite and pyrite.
1924	Keller	Xanthate.
1925	Keller	Scaps for flotation of non- metallics.

Purpose and Scope

The ever increasing importance of the titanium metal inspired this investigation. Titanium compounds are already of great commercial significance, not only as the white pigment of the paint industry, but also in metallurgy, in ceramics and in the electrical industry. The titanium metal possesses many desirable qualities. It is light, strong, tough and non-corrosive. Thus it has the desirable properties of stainless steel and the strong aluminium alloys. These qualities recommend it for many industrial applications. Very desirable gem stones have been produced from titanium dioxides by fusion, cutting and polishing. There are many other uses of the titanium and no doubt many others will be found.

In this research project special attention was given to the selection of a specific selective collector for the titanium dioxides occurring in Ilmenite and Rutile. The orthonitro alkyl phenols having a normal alkyl chain of eight and nine carbon atoms were employed. The work was extended to investigate the effect of a branched side chain alkyl group in this type of flotation collector. Branched side chain alkyl phenols are presently available in commercial quantities at a price which makes their use attractive for the synthesis of the respective ortho-nitro phenols. Previous Work in the Flotation of Titanium Ores

Very little work has been done on the flotation of the titanium minerals. Technical literature reveals that the initial patent by Phelps; U.S. Patent No. 2,257,808, Oct. 7, 1941²⁵ proposed to use of wood creosote, a sodium sulfonated mineral oil, oleic acid or a fatty acid soap to produce a concentrate of iron and titanium ores.

Pickens (24) in 1945 found that a cationic type reagent, a reaction product of thiourea and Schloroethyl oleate, could be used as a collector for titanium bearing minerals. In his work, he ground the titanium ore with 1.5 lb/ton of sodium hydroxide, deslimed by decantations and obtained a rougher silicate float of about 35% solids. These suspended solids were conditioned for five seconds and then floated for two minutes with 0.06 lbs/ton of pine oil and 0.2 lbs/ton of a cationic type collector. The concentrate was then refloated. The rougher tailings combined with the tailings from the float and refloated with 0.12 lbs/ton oleic acid. He obtained Ilmenite concentrate amounting to 56.35% of that in the field; this concentrate contained 52.81% titanium dioxide.

In 1944, McMurray (18) attempted to concentrate by floatation the Ilmenite ore of North Carolina. This ore contains 41.4% titanium dioxide, 32.7% iron oxide and 14.9% (sericite talc) silica gangue. By froth flotation he obtained an 80% recovery. The concentrate product contained 53.85% titanium dioxide, 39.4% iron oxide and 4.8% insoluble. Later on he pretreated a mixture of ilmenite-apatite-silica with starch and depressed the ilmenite with caustic; the apatite was floated off using tall oil as the collector. Then the ilmenite was seperated from this silica, again using tall oil, as the collector.

Moyer (22) recommended the pretreatment of Ilmenite ore low in phosphorous compounds with a depressant such as sodium silicate, sodium hydroxide, and a little calcium hydroxide or silicate instead of starch; apatite separated first, then the Ilmenite.

In later patents, Moyer and McMurray (19) accomplished the selective separation of phosphorous bearing titanium dioxide ore by such collectors as sulfonated free higher fatty acids, resin acids, naphthenic acid, tall oil and the sodium, potassium or ammonium soap of these chemicals. The aqueous pulp mixture is conditioned at a pH six to nine in the presence of an anionic promoter. Caustic, starch, and alkali metal hydroxide may also be used as the conditioning agents.

Recently, a new type of collector has been developed (2) which is particularly applicable to flotation of Ilmenite and other mineral suspensoids, which are negatively charged in the aqueous solution. Characteristic example of this type of reagent is the heavily loaded quarternary ammonium salt,

trimethyl cetyl ammonium bromide; this compound provides a positively charged ion in aqueous solution. Such substances are now generally referred to as cationic agents, in contrast to xanthates and fatty acids, which have the hydrocarbon chain in the anion.

Theory

In the froth flotation, mineral particals should become attached to the inside of an air bubble and be carried to the surface of the pulp where they may become part of the stable froth and be skimmed off with the froth. Taggart (27), Gaudin (14), Wark (30), Peterson (23), DeWitt (6,7) and various other authors (26) have contributed to the literature on the principles and practice of the flotation.

The particular steps involved in the froth flotation separation of minerals are:

- Grinding the ore to a size sufficient to liberate the valuable minerals either one from another or from adhering or enclosing gangue minerals.
- Creation of a buoyant medium (air bubbles) with which to float the valuable minerals.
- Creation of conditions favorable to the formation of a stabilized froth.
- 4. Creation of conditions favourable for the adherence of the mineral particles to air bubbles.

Frothers. The main purpose of the frothing agent is to facilitate the production of a stable froth capable of carrying the mineral load until it can be removed from the flotation machine. (6,30). The frother generally reduces the surface tension of water and thus forms a stable froth (6). There is a wide range of chemicals available for froth formation, but only a few are suitable for flotation purposes. In addition to the property of changing the surface tension, the frothing agent should be cheap, easily available, effective even in low concentrations, and essentially free of the properties of collectors.

Commonly used frothers in flotation are organic compounds. They have chemical structures that are characterized by the presence of two opposing constituents, one part of which is non-polar (hydrophobic) and the other one is polar (hydrophilic). The non-polar group is the hydrocarbon radical having five or more carbon atoms. With few exceptions all good frothers contain only one polar group, the hydroxyl group; examples: pine oil, terpineol, cresol, amyl alcohol, etc.

DeWitt (6) in general states that the frothing agent with the most negative slope of a plot of surface tension versus the metal concentration, shows the most frothing power.

<u>Collectors</u>. The function of the collector reagents is to promote the contact between the mineral particles and air

bubbles by forming a thin coating over the mineral particles, or a complex compound chelate formation, thus rendering it water repellant. Due to the selective action of the collector, the mineral particles become attached to the interface boundary of the air and water and float to the surface in the froth.

The collector should exert specifically selective action on the mineral particles. It should be some what soluble in water, should be stable, non-corrosive, cheap, and easily available.

The chemical structure of the collector is similar in nature to that of the frothers. The polar group should have a specific affinity for the particular mineral. This polar group usually functions on the mineral surface by adsorption, chemical compound formation, or by chelating action. The nonpolar group is the long chain hydrocarbon having six or more carbon atoms.

To explain the behavior of the collector, various hypothesis have been put forward, the outstanding of which are: (1) the chemical (solubility) hypothesis and (2) the adsorption hypothesis but no single theory is yet wholly acceptable for the complete explanation of the flotation phenomena.

<u>Modifying Agents</u>. Under this heading are all reagents whose functions are other than frothing or collecting. Among the more important of these are:

1. Depressing agents:

Since the collector coating is the indispensable

factor in flotation, depressants accomplish their purpose of inhibiting flotation (of unwanted minerals) by preventing the formation of such coating, or destroying it if already formed. The common depressing agents in use are silicates, hydroxides, cynides, and sulfates of the alkaly metals.

2. Activators:

Activators are the substances which so alter the surface of a mineral that it may be filmed by a collector reagent which otherwise would have no effect on that mineral.

3. pH Reculators:

The effectiveness of all classes of flotation reagents depends primarily upon the degree of alkalinity or acidity of the pulp solution, consequently one of the principal object of experimentation is to discover the pH value at which the total effect of the collectors, frothers, and modifying agents will be most favourable for the flotation of a given ore. The common chemicals used as pH regulators are caustic, lime, soda ash, mineral acids, etc.

DESIGN OF THE COLLECTOR

In selection of the collector for the flotation of titanium dioxide containing ore, first consideration should be given to the physical and chenical properties of the mineral. Titanium dioxide is one of a series of oxides combined with various minerals and silica; it occurs either in black, green, or red-brown modification (17). The density of the Rutile is 4.2 gms. per cubic cm. while that of the silica is 2.3 gms. c.c. Therefor the collector must act specifically against the gravity effect. Standard works published by Gaudin (14), Wark (30), and Taggart (27) give the major principles of the flotations and types of collectors used in this research.

The selectivity of the collectors for a specific mineral is of a paramound importance in the flotation of the minerals. The work of the various investigators; Vivan (28), DeWitt (6), Holman (15), Peterson (23), etc. reveals that the collectors may form the chelate or inner complex compounds with the metallic ions. Of the seventy-nine non-frothing collectors studies by Taggart, Taylor, Ince (26), 87.3% have a structure allowing a complex ring closure through combination with a metal atom. According to this view, various analytical reagents and dyes can be used as collectors. Practical economic considerations, however, often preclude such usage.

(10)

The formation of the inner complex ring system depends not only upon the nature of the salt forming or complex compound forming groups with ring closure but to a great extent also on the nature of the metallic ction entering the reaction. Keeping this view in mind, the literature (3, 5, 8, 9, 10, 15, 20, 26, 28, 32) has been consulted for the complex compounds of titanium metal. It was found that the phenols form a complex compound with titanium but they require, to be of use, the presence of ammonia or amines (32) Amino phenols (3) and nitro phenols form titanium complex more readily. On nitration, alkyl phenol gives ortho-nitro phenol (at 0-5°C); the nitro group ortho to hydroxyl group imparts more acidity to the hydroxyl group and hence the resultant compound chelates the titanium atom more readily. This was confirmed by the formation of light coloration when white titanium dioxide powder was mixed with a drop of the concentrated solution of ortho-nitro phenol in absolute alcohol.

Rogler (9) gave the formula Ti (OPh) PhOH to the complex reaction product of titanium dioxide and phenol. It seems more probable that a complex compound of titanium complex with ortho-nitro phenol might be of the nature as:



The crystal structure of the titanium dioxide is (2) tetragonal. Each titanium atom is surrounded with the four atoms of oxygen. Cross linking may occur between the chains, forming plates of titanium dioxide lattices. It seems more likely that in the natural minerals, there will be the intergrowth of the lattice of the other oxides of minerals; moreover some of the lattices may be partly incomplete.

It is furthur suggested, that during the operation of grinding, a fresh rupture may occur between the co-ordinate bond of titanium and oxygen. Thus some of the active metallic atoms may exist at the surface without a co-ordination bond and hence this atom will provide an active centre for the chelation or complex compound formation with the collector. Figure 1 shows such possibility and explains the function of the collectors. Once the chelate compound is formed with the organic collector, its characteristic will be definitely of organic in nature. The hydrophobic alkyl chain will impart a water repellancy. The insolubility of the complex product enhances this water repellancy to a considerable extent. Thus treated the titanium dioxide will float with the collector at the interface boundary, and it will be skimmed off with the foam from the surface.

The extension of this reasoning dictated the choice of the ortho-nitro phenol group coupled with the long alkyl chain. The alkyl group provides the required water repellancy.

EXPERIMENTAL PART

Flotation machine

The flotation machine used in this investigation was a laboratory size, sub-aeration type cell made of lucite. The unit details are shown in the illustrations (fig. 2,3). The agitator was driven by an electric motor. The arrangement was provided for the variation in the agitator speed by various size pulleys. Air was blown under the stirrer by a low pressure blower. The stirrer action broke up the air stream into appropriately sized bubbles.

The overflowed froth was collected on an eight centimeter Buchner funnel; the filtrate from the Buchner was conducted to a suction bottle. The suction bottle was adjusted at such a height, that on cutting of the vacuum, the filtrate was fed into the cell to maintain the constant pulp level. The collector was added to the cell from a burette, having a long curved tip, which made it possible to introduce collector in small portions, at a point well below the pulp surface, where it dispersed readily in the pulp body.

Synthetic ore preparation

The ore and the sand were dry ground in a ball mill: pebbles were used as the grinding media. It is generally most desirable to grind the proper proportion of sand and

(13)



LOO GRAMM - FLOTATION CELL.



FLOTATION CELL.

FIG. NO.3.

ore as a mixture. In this investigation sand and various types of ores were ground separately to avoid contamination. Sand was ground in a one foot by one foot Abbe porcelain ball mill: the titanium ores were ground in a similar small ball mill. The ground material were separated by using Tayler Standard Sieves. The -120 to +200 mesh size was used in the flotation test; the +120 mesh size was reground; and -200 mesh size was rejected. Usually -120 to -200 mesh size is the most desirable size. This state of subdivision effectively liberates the major portion of the mineral particles from the gangue. Finer grinding results in slune formation. Two types of Ilmenite ore, one from U.S.A. and the other from Norway, and one sample of rutile ore (U.S.A) were tested. The major part of the work was done with the rutile sample. Sand used was Ottawa silica sand. After grinding and sizing the sand and ore samples were well mixed. In all runs the charge of the synthetic ore was 100 gms.

Addition of the Reagents

1. Pulp. First about 250 c.c. of water was introduced in the cell and the stirrer was started. Then 100 gms. of synthetic ore was added, keeping enough space for the froth blanket. The pulp was allowed to stirr for seven minutes before the addition of the collector or frother. The higher suspensions in the pulp usually aids the flotation due to the increased apperent density. The optimum solids in the pulp is about 20 to 30% solids.

2. pH Regulators: The reagents used for regulating pH were c.p. hydrochloric acid and c.p. pottassium hydroxide, the latter was a 5% aqueous solution. The conditioning period was ten minutes for each run. All pH measurements were made by using narrow range Hydrion test papers. At least two checks were made for each pH figures.

Frother

The frother used in all runs was a steam distilled pine oil. After the stirring the pulp with the pH regulator for seven minutes, one small drop of pine oil was added, and the stirring continued for two minutes more before the collector was added. The size of the drop of the frother was regulated with the help of a thin piece of wire.

Collectors

One tenth gram of the collector was dissolved in 200 c.c.s of absolute alcohol, which gave a solution containing 0.0005 gms. of collector per milliliter of the solution. The collector solutions were kept in air tight glass stoppered bottles. There was no apparent change in these solutions over a long period of time.

One minute after the addition of the frother, air was allowed to bubble through the pulp for one minute. Then the collector was added in small portions at a time from the burette; after half minute the froth was skimmed off ffom the pulp surface and was collected in the Buchner funnel. The amount of the collector was added over the interval of five minutes during which the froth was collected. With the help of the vacuum, the filtrate was collected in the suction bottle and was recycled to keep the pulp surface at the constant level.

The concentrate was collected on filter paper, and dried on the metal plate, then the concentrate was weighed. The tailings, the remaining portion of the pulp from the cell, were preserved in a bottle. Then the cell, feed and suction bottle and Buchner funnel were cleaned to avoid the effect of the adsorbed collector from the apparatus before starting another run. One cycle of flotation run required about thirty minutes.

Quantitative Determination of the Titanium

In 1949, J. Wandoll (29) found that the titanium bearing iron ores can be fused best by sodium peroxide, but the required quantity of the flux will be eight times more than that of the samples taken. Later on in 1923, (21) Moore and several other chemists of the bureau of mines found that titanium compounds are readily decomposed by fusion with a flux composed of sodium hydroxide three parts and sodium peroxide one part.

One gramm of the dried concentrate sample of the flotation run wasaccurately weighed, and mixed with a flux mixture of sodium hydroxide and peroxide. The mixture was placed in a nickel crucible to be fused. First it was heated slowly and later on the flame was increased. The complete fusion took about thirty minutes. The crucible was covered while being heated.

The fusion mixture was allowed to cool and dissolve in sulphuric acid (1:1). After cooling it was filtered.

Usually Fe, Al, Zn, Cr. Si, Ca and various other elements are accompanied with the titanium minerals. Due to the presence of these minerals, the quantitative determination of titanium is a tedious problem. Das Gupta (4) observed the orange color precipitate with tannic acid and the solution of the titanium compound. Later on he devised the colorometric as well as grevimetric method for the determination of titanium with the help of the tannic acid dolution. Afterwards various modifications have been put forward by various investigators. This modified convenient procedure as follows:

The filtrate (acidic solution H_2SO_4) was diluted to a five hundred milliliters solution with distilled water. Then a fifty to hundred c.c.s solution (which contains about 0.05 to 0.1 gms. titanium) was taken and neutralized with an ammonium hydroxide solution. Next five to ten c.c.s of ten percent aqueous solution of tannin was added, cooled, and diluted if necessary. A twenty percent aqueous solution

of antipyrine was added slowly. An orange colored precipitate was formed. Stirring was stopped and the addition of the antipyrine solution was continued until a white precipitate was formed. Some crystalline ammonium sulfate was added, boiled and filtered. The precipitates were washed with a wash solution containing five percent ammonium sulfate and three percent sulfuric acid.

The titanium complex precipitates were dried, ignited and weighed as titanium dioxides. From the weight of the titanium dioxides and the weight of the concentrate the percentage recovery and concentration were calculated. The results are given in the tables 2,3,4,5,6.

A flux consisting of three parts of sodium hydroxide together with one part of sodium peroxide is the most efficient for the titanium dioxide bearing ores.

A solution containing titanium sulfates forms orange red precipitate with a twenty percent aqueous solution and a ten percent tannin solution. It forms a very bulky precipitate. The precipitate becomes slimy on heating. That limits the quantity of the titanium in the solution. Two to fifty milligrams of titanium in the solution can easily be easily determined. This procedure allows the determination of titanium in the presence of Fe, Al, Cr, Co, Mn, Ni, P, Si, Zn, etc. without the separation of it. Thus it gives fairly accurate results. The following designations are used for the different collectors:

- 1. 2-Nitro 4 n-Octyl phenol N 8.
- 2. 2-Nitro 4 n-Nonyl phenol N 9.
- 3. 2-Nitro 4 Octyl phenol (commercial) .. C 8.
- 4. 2-Nitro 4 Nonyl phenol (commercial) .. C 9.

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TABLE 2.

FLOTATION OF RUTILE BY: 2 Nitro 4 n-octyl phenol.

(Figures: 4-6)

Synthetic ore: 100 gramms. 1.96% TiO₂. Time of the run of experiments: 5 minutes.

Synthetic ore size: minus 120 mesh.

•

pH	Collector	Concent	trates	Enrichment	Recovery
	#/ton.	gramms	%T102		%
3	•2	18.60	6.40	3.35	60.9
7	.2	18.13	8.03	4.29	66.2
10	•2	12.13	14.23	8.13	88.2
3	.1	16.53	4.63	2.42	39.1
7	.1	13.82	10.10	5.5	71.5
10	.1	18.06	7.33	3.88	67.5
3	•05	8.92	8.23	4.4	37.5
7	•05	9.58	8.88	4.45	43.5
10	.05	8.98	9.38	5.07	43.0

TABLE 3.

FLOTATION OF RUTILE: BY 2 Nitro 4n-Nonyl Phenol. (Figures: 4-6.)

Synthetic ore: 100 gramms. 1.96% TiO₂. Time of run of the experiments: 5 minutes. Synthetic ore size: minus 120 size.

рH	Collector.	Concentrates		Enrichment	Recovery	
	#/ton	gramms	%T102		Ø ø	
3	.2	4.88	12.83	7.22	32.0	
7	•2	10.64	13.73	7.75	75.0	
10	•2	12.35	14.13	8.07	89.1	
3	.1	7.10	7.88	4.19	28.6	
7	.1	7.93	10.33	5.65	41.8	
10	.1	8.94	14.23	8.11	67.2	
3	•05	10.82	5.93	3.09	32.5	
7	•05	10.07	7.48	3.96	36.3	
10	•05	5.65	8.08	4.31	23.2	

TABLE 4.

FLOTATION OF RUTILE BY: 2 Nitro 4-Octyl phenol. (Commercial.)

(Figure 4-6.)

Synthetic ore: 100 gremms. 1.96 % TiO₂. Time of run of the experiment: 5 minutes. Synthetic ore size: minus 120 size.

pН	Collector.	Concentrate		Enrichment	Recovery	
	#/ton	gramms	% T 10 ₂		K	
3	.2	10.96	9.02	4. 86	50 .6	
7	•2	14.94	8.03	4.28	61.3	
10	.2	13.21	13.73	7.81	92.8	
3	.1	10.45	12.33	6.9	68.5	
7	.1	9.81	14.78	8.5	74.0	
10	•1	9.68	14.03	8.0	69 .4	
3	•05	3.56	9.43	4.84	17.1	
7	.05	4.02	11.83	6.58	24.3	
10	•05	5.63	12.68	7.12	36.4	

TABLE 5.

FLOTATION OF RUTILE BY: 2 Nitro 4 Nonyl phenol. (Commercial)

(Figure 4-6)

Synthetic ore: 100 gramms. 1.96 % TiO₂ Time for the run of experiments: 5 minutes. Synthetic ore size: minus 120 mesh.

рН	Collector.	Concentrate		Enrichment	Recovery	
	#/ton	gramms	%TiO ₂		%	
3	.2	10.90	8.76	4.71	49.0	
7	•2	14.95	7.88	4.14	60.2	
10	•2	12.62	11.27	6.23	72.4	
3	.1	8.87	8.93	4.8	40.4	
7	.1	8.27	16.23	9.5	68.8	
10	.1	8.19	15.13	8.74	64.0	
3	•05	11.54	8.23	4.4	48.6	
7	.05	11.97	10.68	5.85	64.0	
10	•05	8.12	9.38	5.07	38.8	

TABLE 6.

FLOTATION OF Ilmenite & Rutile ore Samples.

Collectors: N 8, N 9, C 8, C 9.

Synthetic ores: 100 gramms.

Synthetic ore size: minus 120 mesh.

Time for the runs of the experiments: 5 minutes.

Sample p	H	Collector	T102	Concentrates		Enrichment	Recovery	
			%	gramms	%		%	
Rutile	7	N 8	4.75	9.85	29.5	8.42	61.1	
		C 8		12.59	27.6	7.67	73.0	
		N 9		10.41	28.6	8.05	62. 8	
		C 9		17.05	20.7	15.25	74.4	
1	0	N 8		9.98	43.0	15.17	90.4	
		C 8		16.08	26.85	7.37	90.9	
		N 9		14.17	31.7	9.32	94.7	
		C 9		12.52	30.35	8.8	80.0	
Ilmenite	10	N 8	3.29	15.32	20.6	7.64	95.8	
		C 8		13.76	21.0	7.81	90.2	
		N 9		15.95	20.0	7.35	97.0	
		C 9		11.98	24.8	9.7	92.5	
Ilmenite	10	N 8	4.21	19.67	20.7	5.95	96.7	
		C 8		14.56	26.6	8.25	92.0	
		N 9		18.56	19.6	5.55	86.6	
		C 9		16.48	23.8	7.42	93.1	



FIG. 4.







FIG. 6.

Discussion of the Results

Examination of the tables two to five and figures 4, 5, 6, indicates the general trends of the effect of the various variables in the several flotations. Each series of tests shows both enrichment and the recovery of the titanium dioxides ores from the synthetic mixtures. This enrichment and recovery is due to presence of the collectors tested. Blank runs without collector gave very little enrichment and recovery. The effect of the carry over and adhered collectors in the successive runs is avoided by flushing the whole unit with fresh water.

<u>PH of the pulp</u>. Percent recovery and percent enrichment is found to be a function of the PH value of the pulp. The general trend is shown in the figures 4,5,6. It is found that the higher the PH, the higher is the recovery. At higher PH the amount of frother required is smaller. It was noticed that even a very small excess of the frother tends to form a considerable large amount of froth which entangles almost all particles of the pulp. A pH of eight or ten is the most economical for the flotation of the titanium bearing ores.

<u>Collectors</u>. An increase in the amount of collector at higher pH increases the percent of recovery as well as percent of enrichment. The major test runs were carried out with the Rutile sample U.S.A. The Rutile samples tested were already well crushed. Very little grinding was required for the required sizing in the flotation runs. The sandy sea shore ore requires more of the collector! The test series results show good results with 0.1 to 0.2 lbs. of ore or mixture per ton of collectors.

The results of the ore samples containing higher concentration of the titanium dioxides, are given in table No. 5. Three synthetic ore samples were studied. The latter two samples were of the freshly crushed and ground Illmenite ores. In these runs it was observed that the color of the pulp body cleared up in about two minutes. After two minutes the froth collected contained a very small quantity of the titanium. Thus it appears that freshly crushed ores require very small amounts of the collector. The recorded results were obtained at pH 10 with 0.2 lbs. of collector per ton of ore mixture. Higher percentages of the recovery and enrichment are observed under these conditions.

<u>Type of the alkyl chain</u>. It is obvious that the increased number of carbon atoms in the alkyl chain increases the water repellancy of the collector and as a result longer chain alkyl collectors give better results. Two normal alkyl chain and two branched chain alkyl compounds were studied. The commercial octyl phenol had branched chain as: FiG. 7.

The results with these chemicals as collector show very little difference. It seems that as long as the branched alkyl chain does not occupy more cross section that that of the benzene ring including the groups which form the chelate or complex ring formation with the titanium atoms good flotation results are observed. If the side chain is longer and occupies more cross section, then it tends to reduce the collecting effect to a certain extent.



FIG. 7.

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CONCLUSIONS

The following conclusions are drawn from the data presented.:

1. It is shown that the 2 Nitro 4 Alkyl phenols function as the specific collectors for Rutile and Ilmenite in the synthetic mixtures of titanium dioxides with the quartz sand. Ortho position of the nitro group to the hydroxyl group increases the acidity of the hydroxyl group. Thus it seems that it forms the chelate ring (complex formation) with the titanium atoms of the titanium lattices.

2. The alkaline condition favours the flotation of the titanium ore. The pH eight to ten appears to be most favourable for the titanium dioxide flotation with the 2 Nitro 4 Alkyl phenols as the collectors. O.1 to 0.2 pounds (of the collector) per ton gives 70 to 90 % recovery and an enrichment of seven to fifteen.

3. This technique can be used to process the sea shore sands containing titanium dioxide. These freshly crushed and ground ores give much better recovery even with a smaller amount of the collector.

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APPENDIX

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The Synthesis of 2 Nitro 4 Alkyl phenols

The reactions involved are as follows:



Anisole ketone was prepared according to Fieser L.F. and Hershberg E.B. (10). One mol (108 gms.) of anisole was taken in a three necked flask, fitted with a mechanical stirrer, a reflux condensor and a thermometer. 600 ccs. of tetrachloroethane was added as solvent and cooled to 5° C by an external cooling with an ice-salt mixture. 1.2 mol of hexanyl chloride (161 gms) were placed and mixed well with mechanical stirrer. While stirring 1.4 mol of anhydrous aluminium chloride (187 gms) were added gradually over a period of three hours. The reaction temperature was maintained at 4 - 8° C. After addition of anhydrous aluminium chloride, the reaction mixture was allowed to stirr for a half hour more. The red reaction mixture was allowed to stand for three days at room temperature.

The fatty acid chlorides were prepared according to the method of Armour Chemical company (31).

After three days, the reaction mixture was poured in a four litre beaker containing cracked ice and hydrochloric acid. Brownish precipitate separated out when the reaction mixture was allowed to stand a few hours. The tetrachloroethane layer was separated. Then it was extracted with 1200 cc's. of diethylether. The ether extract was treated with concentrated sodium carbonate solution. The ether extract was distilled to boil off the ether, tetrachloroethane and unreacted anisole. The residue was treated with the hydrochloric acid as follows: (16).

The residue was taken up in the three necked flask. The stirrer a reflux condensor and the thermometer were provided to the flask. One mol of 48% hydrobromic acid was

added in it. It was heated externally, and allowed to reflux for three hours. To avoid bumping it is desirable to stir continuously. Next day, the excess hydrobromic acid was boiled off. The residue subjected to the Wolfe - Krishner reduction (20).

In a three necked flask, the above residue was placed with 1500 ccs. of diethylene glycol, 190 gms. of potassium hydroxide and 130 ccs. of hydrazine hydrate. While stirring the mixture was refluxed for $l\frac{1}{2}$ hours. Then the condensed water was allowed to be removed until the temperature of the reaction mixture reached to 195° C. At this temperature it was refluxed for four more hours. Then it was acidified by adding concentrated hydrochloric acid. The mixture was extracted with 2000 ccs. of benzene. The benzene extraction solution was evaporated to remove benzene. The resulting product was vacuum distilled.

No.	Compound.	B.P.	at pressure.
1.	4 Octyl phenol.	130-140° C	6-8 mm. Hg.
2.	4 Nonyl phenol.	140-145 ⁰ C	6-8 mm Hg.

Nitration

The nitration procedure followed, is similar to that of Cecil M. Galloway (11).

0.17 mol of octyl phenol was dissolved in 80 ccs. of benzene and the dissolved mixture was taken into the dropping funnel. 0.18 mol of nitric acid with 12 mol of water was placed in the three necked flask. The acid mixture was stirred with the mechanical stirrer, and the solution of alkyl phenol was added drop-wise from the dropping funnel. The reaction mixture was maintained at a temperature $5 - 10^{\circ}$ C with the external cooling with the cracked ice and salt mixture. After addition the reaction mixture was stirred for a half hour more. The reaction mixture was diluted with water, and benzene layer was separated. The benzene was distilled off, and the residue was vacuum distilled.

The same procedure was followed for the nitration of the commercial p - alkyl phenol.

	Collector.	Type B.P. at pressure
N 8	2 Nitro 4 Octyl phenol.	Normal 152-158°., 5 mm. Hg.
N 9	2 Nitro 4 Nonyl phenol.	Normal 172-176 ⁰ C, 9 mm. Hg.
C 8	2 Nitro 4 Octyl phenol.	Commercial 125-127 ⁰ C, 5mm. Hg.
C 9	2 Nitro 4 Nonyl phenol.	Commercial 138-147° C, 5 mm. Hg.

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