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# A STUDY ON THE PRODUCTION OF ANTIMONY TRIOXIDE FROM ITS ORES BY VOLATILIZATION PROCESS AND ITS PROPERTIES

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MARKO KOHEN

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# A STUDY ON THE PRODUCTION OF ANTIMONY TRIOXIDE FROM ITS ORES BY VOLATILIZATION PROCESS AND ITS PROPERTIES

## I. INTRODUCTION

This thesis is a report on the study made on the production of antimony trioxide from its ores by volatilization process. A study is also made for the determination of the properties of the antimony trioxide thus produced. The process was mainly to roast the antimony sulfide containing ore, at temperatures above the volatilization temperature of antimony trioxide (330 °C), and to collect the fumes produced.

Antimony trioxide is a white pigment, which is used in paints, enamels, lacquers, printing inks, and in paper. Until the introduction of chalking-resistant and fading-resistant grades of titanium dioxide in 1941, antimony trioxide was the leading white pigment in the market. The principal reason for the adoption of titanium dioxide was its lower cost.

Turkey has sources of antimony ore. The total reserve in Turhal area is estimated to be 155,000 tons of ore[29]. There is also another deposit in the vicinity of Eskigümüş near Niğde. But there are no titanium deposits in Turkey. The titanium dioxide used in the industry is all imported. But antimony trioxide can be produced in Turkey. This, will cause foreign currency savings, and will also reduce or eliminate the price difference between antimony trioxide and titanium dioxide, since the price of the latter is made more than twice expensive trough importation procedures.

With this aim in mind, an apparatus was assembled in the laboratory to produce antimony trioxide from local ores. The process variables, such as, air volume and temperature were studied to find the optimum conditions for the production of the best grade of antimony trioxide. The product was tested for its pigment properties and these were compared with the properties of commercial titanium dioxide and lithopone, two widely used white pigments. The fire retarding property of antimony trioxide, which was discovered during World War II, was also studied. This discovery has a great technical and economic significance. This property of antimony trioxide was tested by preparing a polyvinylchloride composition containing 8 per cent antimony trioxide and comparing its burning properties with an ordinary polyvinylchloride composition.

The results obtained have shown that under carefully controlled conditions pigment grade antimony trioxide can be obtained by volatilization process.

## II. PRODUCTION OF ANTIMONY TRIOXIDE

### A. Literature Survey

The production of antimony trioxide by volatilization process was proposed by Bobierre, de Ruobz and Rousseau[23] in 1844, and this idea was applied by de Fraceschi, Glass, Herrenschmidt, Oehme, Herring, Helmhacker, Chatillon, Woolford, Plews, Rasse-Courbert, and the Miniere e Fonderie d'Antimonie Socièta Anonima, Genoa, Italy[23]. The process of manufacturing antimony trioxide on a commercial scale is in many ways similar to that used for the manufacture of zinc oxide. In the volatilization process, the ore is treated at high temperatures to burn the sulfur away and the volatilized antimony is collected. In this process the sulfur in the sulfide first burns to sulfur dioxide and then with rise in temperature the antimony burns to antimony trioxide. The sulfur ignites at a temperature near 200 °C and the antimony at about 300 °C[8].

There are many variations of the volatilization process, the principles employed being the same but the equipment differing. Hering[8] used a reverbatory furnace for roasting while Plews[8] used a rotary furnace heated with an oil or gas blast. The furnace suggested by Chatillon consists of two rectangular cupolas charged with ore and these cupolas communicate with two smaller cupolas where hot air is produced and where the last traces of antimony trioxide are produced[23]. The volatilization process is also accomplished in a Herrenschmit or stack furnace. This furnace consists of a rectangular shaft which is fitted with a step-grate of iron bars[8]. The upper part of the furnace communicates with an oxide chamber, a series of condensing chambers provided with condensation tubes of corrugated iron, and finally with a bag chamber[8,23]. The air and dust are drawn through these chambers by an exhaust fan. If the stack furnace is properly designed, so that the temperature in the central portion of the ore does not produce caking from fusion and if the depth of the combustion zone is so regulated that the antimony in the ore is completely volatilized its efficiency would be high. These results are obtained if the furnace is relatively deep and not too large in diameter and if the area increases with the depth so that in case of fusion the ore is not held up by the side walls.

The oxide is recovered in flues, condensing pipes, a baghouse, Cottrell precipitators, sheet iron tanks acting as a filtration chamber, hopper-bottom baffle-plate type collection chambers or in combinations of these[4,8,15,23]. The use of a water scruber in the recovery of antimony trioxide is only to be recommendend, where other means of collection fail to function. The reason for this is that the oxide is not marketable in the wet state and it is a very difficult product to dry[8]. After it is dried, it will be in the form of a dry cake that must be finely ground before it can be used. The bag house consists of a number of annular compartments, each containing 12 bags for the collection of antimony trioxide[20]. The antimony trioxide-ladden air enters the baghouse at the bottom of the compartment, making a sharp turn in entering the lower ends of the bags, and thus tending to cause the larger particles to drop into the hopper. The upper ends of the bags are closed, the air passes through the interstices of the cloth, and the product is collected on the cloth fibers. The bags are cleaned by a violent shaking, the product dropping into the dust hopper and at the same time a current of gas is passed through the bags in the opposite direction to aid the bag cleaning. The bags are usually made from muslin or woolen cloth[4]. Cottrell precipitators seem to be very successful for the recovery of antimony trioxide. The process is very simply carried out by suspending a series of wires in a series of pipes and through these the air carrying the antimony trioxide particles is allowed to pass[20]. A high voltage is then applied between the wires and the tubes and as a result all the suspended particles are attracted to the sides of the pipe and held there. This phenomena is based on the fact that a gas stream, and particles suspended in it, become charged or ionized when passed between electrodes producing a strong electrical field[20].

## B. Raw Materials

The raw materials required for the production of antimony trioxide are; antimony ore, fuel, and air.

### 1. Antimony Ore

The terrestrial abundance of antimony is approximately 1 gram per metric ton[15]. Antimony rarely occurs in its native form. It occurs as Stibnite ($Sb_2S_3$), Jamesonite ($Sb_2S_3$. 2PbS), Kermesite ($2Sb_2S_3.Sb_2O_3$), Valentinite ($Sb_2O_3$), and Senarmonite ($Sb_2O_3$)[4,21]. The most important ore of antimony is Stibnite. Stibnite has a low specific gravity (4.5-4.6) and is very soft[21]. It has been stated that[2]; the mining of antimony veins differs in no way from that of ordinary quartz veins containing base metals, and seldom presents any special difficulties. The ore as mined may be low grade but it can be concentrated by hand sorting and floatation. In another process, called liquation, the crude sulfide is melted in such a way that the molten sulfide flows away from the less fusible rocky impurities[4,19].

Antimony ore poduction of Turkey is sumarized in Table 1.

TABLE 1

ANTIMONY ORE PRODUCTION OF TURKEY

| YEARS | PRODUCTION (TONS)$^{+}$ | VALUE (TL)$^{+}$ |
|---|---|---|
| 1963 | 2940$^{++}$ | -- |
| 1964 | 2899$^{++}$ | -- |
| 1965 | 3237$^{++}$ | -- |
| 1966 | 3310$^{+++}$ | 7,486,848$^{+++}$ |
| 1967 | 2620$^{+++}$ | 6,352,092$^{+++}$ |
| 1968 | 2290$^{+++}$ | 5,596,713$^{+++}$ |

+- A mixture of ores containing 40, 50, and 60 per cent Sb.
++ Data taken from "Maden İstatistikleri"[30] bulettin.
+++ Data taken from the "Türkiye Madenciler Cemiyeti"[33].

In our contacts with the "Türkiye Madenciler Cemiyeti"[33] we were also informed that there is a large amount of low grade ore (approximately 15 per cent antimony) which is not mined because there is no market for such ores. But these ores can be utilized for the manufacture of antimony trioxide by volatilization process.

## 2. Fuel

The overall reaction, during the volatilization of antimony trioxide is exothermic as shown below:

$$2Sb_2S_3 + 9O_2 = 2Sb_2O_3 + 6SO_2 \qquad H=-340 \text{ kcal/mole } Sb_2S_3$$

Therefore the fuel requirement is not great. The fuel can be any fuel which will fit the apparatus used. For low grade ores which do not contain enough antimony and sulfur to maintain the volatilization temperature in the furnace, some coke is added with the charge. For an ore averaging about 10 per cent antimony content, 4 per cent of coke is charged with the ore[8].

### 3. Air

Air is supplied either by a compressor or by a vacuum pump. The former is installed right before the reactor and the latter is installed after the collecting part. The choice of either one is made according to the apparatus used.

## III. PROPERTIES OF ANTIMONY TRIOXIDE

### A. Properties of Antimony Trioxide as a Pigment

### 1. White Pigments in General

Before going into the details of the properties of antimony trioxide as a pigment, it will be better to review the significance of the general properties of the white pigments. Free solubility in water or oil and instability at ordinary temperatures are about the only properties which would render a white substance entirely unsuitable for use in paints[6]. But a pigment must posess also other properties except the insolubility in water and oil and stability at ordinary temperatures, before it can be acceptable. Modern paints are used for four purposes. They are used: for decoration, for the protection of structural materials, for sanitation, and for obtaining better distribution of light or greater illumination. Paints were first used for their esthetic appeal. The other functions were later required by the conditions and they were adopted in the order presented above. As a consequence these new functions imposed new conditions on the pigments. A certain fineness of particle is obviously necessary before a mixture of pigment can be uniformly spread over a surface with a brush, as very coarse particles will naturally settle out quickly from the oil. But this is not the only consideration which requires fine subdivision. The spreading power of a pigment is measured by the greatest area over which a unit mass of a substance, mixed to a painting consistency with a given medium, can be uniformly spread with a brush[6]. Obviously finer subdivision will increase the spreading power of the pigment. The hiding power of a pigment, which is the ability of the pigment mixed with a given medium to painting consistency to obscure or cover a colored design, is also increased by increasing fineness[6,22]. Although the various factors determining the "optimum particle size" for hiding are not a matter of agreement among authorities, a white pigment with a diameter of 0.2 to 0.3 microns can be considered to give the maximum hiding[22]. Among the important factors influencing the hiding power of a pigment is the ratio of its refractive index in air to the refractive index of the vehicle to air. And since for a given mass of a pigment the refractive index depends on the total area of contact-surface (medium to pigment) exposed to light, the refractive index is a function of the size of the seperate particles[6]. Another consideration which is closely related to the fineness of a pigment is the luster of a paint. Luster is judged by the extent to which a surface can serve as a mirror. Luster is divided into two factors: gloss and sheen, the former being measured at 45° or 60° and the latter at 75° or 85° angle by a reflectometer[4]. A paint cannot dry with a gloss unless the liquid medium forms a continuous phase. Therefore it is apparent that fineness of the particles is required so that the texture becomes more uniform and the particles are completely covered with an envelope of oil. The quantitative observation of the amount of oil necessary to form a mixture of painting consistency, namely the oil absorption of the pigment, is a guide to the fineness of the particles. The oil absorption, however, is not only dependant on the particle size of the pigment. Differences in oil absorption are also caused by the difference of the respective surface energies of the pigments in oil[6]. Even though the hiding power, spreading power, the luster and the oil absorption of a pigment are improved with increasing fineness, the opacity of the paint is reduced. Increasing fineness does not effect the total volume per unit mass of a pigment. But the surface area for a given volume increases with increasing fineness. Thus the finer the particles the bigger is the amount of oil required to envelope them. The increase in the amount of oil will decrease the ratio of the pigment volume to the paint volume, which means decrease in the opacity of the paint. But in practice a pigment must yield a sufficient opaque mixture in oil, otherwise labor costs in application of extra coats become prohibitive. All these requirements are summarized in the definition of the ideal pigment as defined by Clarke[6], which states that: The ideal pigment is a substance of high refractive index, whose particles while carrying only thin envelopes of oil, can flow readily over one another. The particles should be small enough to ensure the smooth texture and good spreading power. They should not prohibit glossiness in a normally brushed-out coat on glass. With this physical requirements must go chemical stability under ordinary climatic changes and chemical inertness to paint media.

## 2. Antimony Trioxide

After having reviewed the general properties of the pigments we now can go into the study of antimony trioxide. Antimony trioxide of the type specially prepared for use as pigment is an extremely white powder. It exists in two crystalline forms; cubic and orthorhombic[25]. The cubic form is inferior to the orthorhombic form because of its lower density and its instability at higher temperatures. The cubic lattice can accept extra oxygens and turn into more stable higher oxides, namely, $Sb_2O_4$ and $Sb_2O_5$[25]. The specific gravity of the cubic antimony trioxide is 5.2 and of the orthorhombic antimony trioxide is 5.76[25]. But there are other values reported for the specific gravity of antimony trioxide in the literature. Mathiello[13] and Clarke[6] report the specific gravity of antimony trioxide as 5.73 and 5.4 respectively. Antimony trioxide melts at 1212.8 °F (656 °C) and boils at 2822 °F (1550 °C)[13]. Irrespective of its way of production antimony trioxide is a fume product, therefore its particle size averages less than one micron. The commercial $Sb_2O_3$ has three grades, which vary in color and texture. These grades are commercially known as; White Star, Red Star, and Green Star. White Star, the whitest grade, compares favorably in brighness to the highest grade competitive pigments[13]. Red Star is of very white color but not as bright as White Star. Green Star poseses a pale ivory cast. The chemical compositions of these three grades are represented in Table 2.

TABLE 2
COMPOSITION OF THE THREE GRADES OF
ANTIMONY TRIOXIDES[13]

| | WHITE STAR | RED STAR | GREEN STAR |
|---|---|---|---|
| $Sb_2O_3$ | 99.85 | 99.65 | 99.60 |
| $Sb_2O_4$ | 0.15 | 0.30 | 0.40 |
| $Fe_2O_3$ | 0.0001 | 0.0002 | 0.00025 |
| PbO | 0.0006 | 0.0006 | 0.0006 |
| $As_2O_3$ | 0.0037 | 0.009 | 0.0130 |
| S, Cu, Bi, Zn | Nil | Nil | Nil |

The common white pigments are in two well defined categories: (a) those which serve primarily to add durability to the paint layer (white lead, zinc oxide) and (b) those which are primarily opacifiers with superior hiding power (titanium dioxide, lithopone)[25]. Antimony oxide occupies a position between two classes; it is superior to white lead and zinc oxide in hiding power, and shows a greater durability than the opacifiers such as titanium dioxide.

TABLE 3

HIDING POWER OF WHITE PIGMENTS[27]

| PIGMENT | HIDING POWER Sq. ft. per lb. | HIDING UNITS |
|---|---|---|
| Basic lead carbonate | 15 | 1.00 |
| Basic lead sulfate | 13 | 0.87 |
| Zinc oxide | 20 | 1.33 |
| Zinc Oxide (35 % leaded) | 20 | 1.33 |
| Lithopone | 27 | 1.80 |
| Antimony trioxide | 40 | 2.67 |
| Titanium barium pigment (A) | 40 | 2.67 |
| Titanium barium pigment (B) | 46 | 3.07 |
| High strength lithopone | 44 | 2.93 |
| Titanated lithopone | 44 | 2.93 |
| Titanium calcium pigment | 48 | 3.20 |
| Titanium magnesium pigment | 47 | 3.13 |
| Zinc sulfide | 58 | 3.87 |
| Lead titanate | 60 | 4.00 |
| Titanium dioxide | 115 | 7.67 |

As stated before, the hiding power of pigments is a function of the refractive index of the pigment with respect to the oil medium. The refractive index of antimony trioxide lies between the "protective" pigments and the "opacifier" pigments, as shown in Table 4.

Antimony trioxide pigment, due to its high refractive index, pure white color, fineness of particle size and ready dispersion is used as an opacifier in paper industry. If the air spaces in an unpigmented sheet are filled with a printing ink which has an index of refraction around 1.50, the sheet becomes translucent or even transparent. This is due to the fact that, 1.50 is very near to the refractive index of the cellulose fibers, which is 1.53[4]. However, paper pigmented with antimony trioxide, which has an index of refraction considerably greater than that of the printing ink vehicle will maintain the high degree of opacity so that "show through" will be prevented.

TABLE 4

REFRACTIVE INDICES OF SOME WHITE PIGMENTS[22]

| PIGMENT | | REFRACTIVE INDEX | AUTHORITY |
|---|---|---|---|
| Basic carbonate white lead | | 1.94-2.09 | Merwin |
| Basic sulfate white lead | | 1.93 | Merwin |
| Zinc oxide (ZnO) | | 2.02 | Merwin |
| Titanium oxide ($TiO_2$) | Rutile | 2.76 | I.C.T |
| | Anatase | 2.55 | T.P.C. |
| Barytes ($BaSO_4$) | | 1.64 | Merwin |
| Calcium sulfate | | 1.59 | I.C.T. |
| Antimony oxide ($Sb_2O_3$) | | 2.09-2.29 | I.C.T. |
| Silica ($SiO_2$) | | 1.55 | I.C.T. |
| Zirconium oxide | | 2.40 | Andrews |
| Lead titanate | | 2.7 | T.P.C. |
| Diatomaceous earth | | 1.45 | Dicalite Co. |
| Whiting | | 1.60 | I.C.T. |

Enamels are decorative and protective glassy coatings on metals. The most common cover enamel has been the white cover coat. Whiteness or high diffuse reflectance has been called opacity in porcelain enamel terminology[14]. Opacifying crystals are those crystals whose index of refraction is much different from that of the glass, which is in the range of 1.50-1.55. The most effective opacifiers are given in Table 5.

Prior to the introduction of titanium dioxide as an opacifier for enamels, the most common opacifiers were antimony trioxide and zirconium oxide. Today, all three are used in combination or separately. Spectrophotometer curves for enamels opacified with oxides of antimony, zirconium and titanium are shown in Figure 1. The spectrophotometer curves for these three enamels indicate the characteristics of a bluish white color, which is the most desirable color in white-cover enamels[14].

TABLE 5

MOST EFFECTIVE OPACIFIERS IN PORCELAIN ENAMELS[14]

| OPACIFIER | INDEX OF REFRACTION |
|---|---|
| NaF | 1.336 |
| $CaF_2$ | 1.434 |
| $Sb_2O_3$ | 2.087-2.35 |
| $SnO_2$ | 1.997-2.093 |
| $ZrO_2$ | 2.13 -2.20 |
| $TiO_2$ (anatase) | 2.493-2.554 |
| $TiO_2$ (rutile) | 2.616-2.903 |

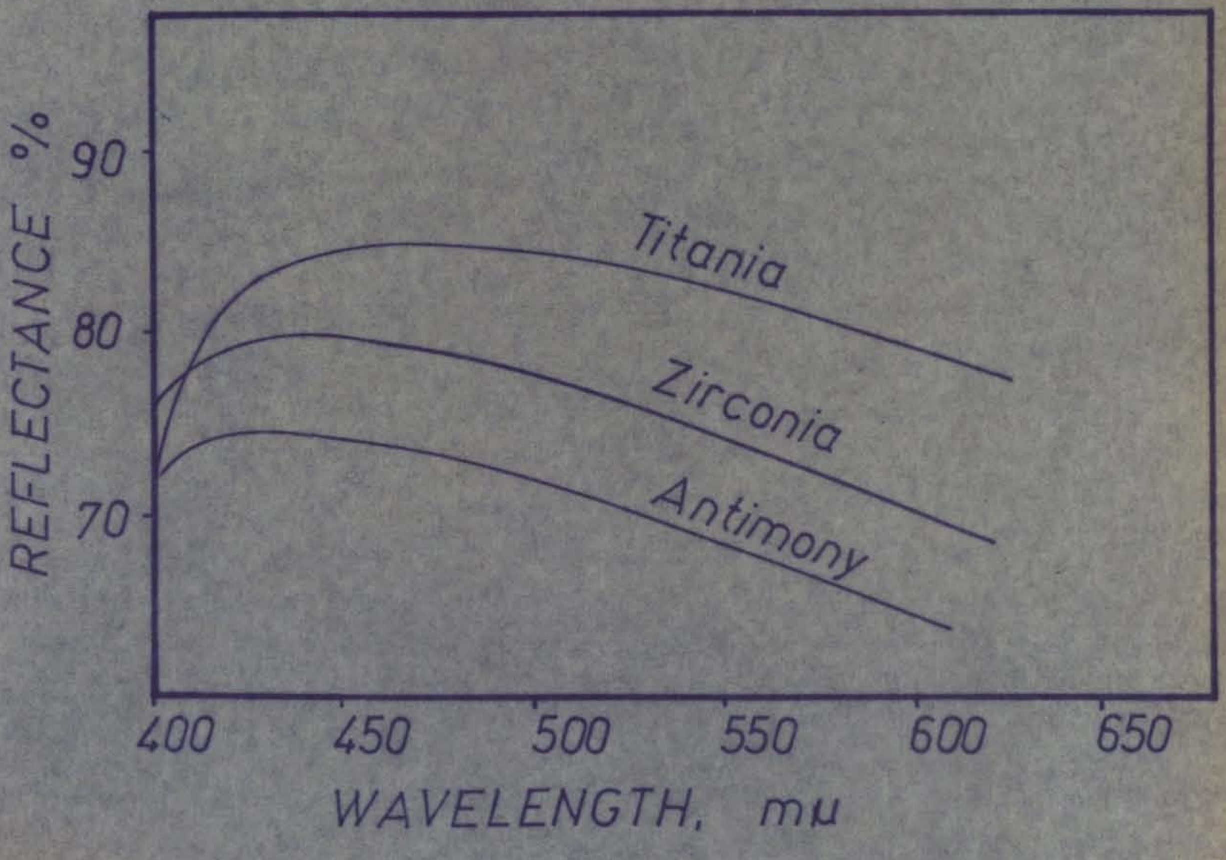

Figure 1: Spectrophotometer Curves for Titania, Zirconia and Antimony Enamels[14]

Chalking is the presence of a loose powder, evolved from a paint film itself at or just beneath the surface. Very light, especially white, paint films which do not chalk, become dirty and discolor quite rapidly, while white paint films which chalk maintain color much longer, although they loose gloss progressively[16]. Colored films which contain white pigments may show a color fading when chalking begins. This is due to the masking effect of the white chalky surface. Excessive chalking reduces the life time and decorative value of the paint. But, when it is considered that, the non-chalking paints discolor rapidly due to dirt collection, or become brittle and crack, moderate chalking seems to be more advatageous[16]. Among white pigments and extenders such as; chalk, zinc sulfide, various grades of lithopon, titanium whites and antimony trioxide, antimony trioxide has the smallest tendency to chalk in open[16]. Antimony trioxide chalks slowly and uniformly, holds its tints and color well, and minimizes cracking. For this reason, relatively large quantities of this pigment are used in the manufacturing of high-grade automative finishes, where high-gloss, durable, and permanent coatings are demanded[13]. The quantity of antimony trioxide used for enamels and lacquers of this kind varies from 25 to 60 per cent of the total white pigment base[13].

"A lacquer is a colloidal dispersion or solution of nitrocellulose, or similar film forming compound, resins and plasticizers in solvents and diluents, which is used as a protective and/or decorative coating for various surfaces and which dries principally by evaporation of its volatile constituents"[30]. Antimony trioxide is extensively used in lacquers. It is found to be excellent for exterior lacquer enamels, where it is used alone or with zinc oxide and titanium dioxide to decrease the chalking tendencies[13]. It has very good color retention on exposure.

Antimony trioxide is inert to the oily medium used in paints and it is readily wetted by oils[6,13, 25]. Its dispersive properties are good, and there is no tendency to form coarse aggregates in paint media. It is one of the very few pigments that can be incorporated directly into the oily medium simply by stirring. It has low oil absorbtion, and a good paste can be ground containing 10 per cent of oil[6,25]. From such pastes it is possible to prepare oil-paints containing as much as 78 per cent pigment, which flow well under the brush and give coats of great opacity and purity of color[6].

Antimony trioxide paints are attacked by hydrogen sulfide in the presence of moist air[6,13]. In the presence of moist hydrochloric acid, they become sensitive to hydrogen sulfide and turn yellowish. But these are not normal atmospheric conditions. Clarke[6] reports an experiment conducted in Tyneside. The exposure of Antimony trioxide coats, over two years period, to the industrial atmosphere at Tyneside produced practically no cracking and very little chalking and the color was not effected. Under the same exposure conditions white lead coats turned brown. Tests have proved that the addition of a small amount of zinc oxide to the antimony trioxide definitely prevents the discoloration due to hydrogen sulfide, because zinc oxide has a preferential absorption for hydrogen sulfide, forming zinc sulfide, which is white[6,13]. One to five per cent zinc oxide by weight, based on the antimony trioxide content, has been shown to be sufficient under ordinary conditions of exposure[13].

Antimony trioxide has no accelerating effect on the drying of linseed oil. This defficiency is readily overcome by incorporating a small amount of drier to the paint. The drier may be of any type used for paints. Very satisfactory results have been obtained with equal parts of yellow litharge and manganese borate ground first in linseed oil and added in the proportion of one part of the mixture (dry weight) to 100 of antimony trioxide[6]. Paints containing about ten per cent zinc oxide and two per cent cobalt linoleate have also given good results[6]. The addition of cobalt driers to paints containing antimony trioxide causes the dried film to have a greenish tint. When manganese is used in conjunction with cobalt it produces a film having a slightly pink tone. The use of linseed oil boiled with 1/2 per cent of chromium phosphate yields an extremely pale product.

There is a great confusion in the literature, with respect to the toxicity of antimony trioxide. Dernehl et al[9] reports a toxicological study made with inhaled antimony trioxide. In their experiments, the mortality rate among guinea pigs which have inhaled 13-424 milligrams of antimony trioxide was found to be 13 per cent. In the exposed animals there was a decrease in the white-blood cell count and death from pneumonia was more frequently encountered. Hess[17] states that pigments or paints containing antimony are toxic in the sense of the law "Poisons Act and Statuary Rules and Order, 1935, No. 1239 ". However, he also states that; there are no general regulations against its use in the paint and varnish trade and for industrial purposes with the exception of the food and related industries. Clarke[6], Mathiello[13], and Newton et al[25] consider antimony trioxide as a non-toxic pigment.

"All in all antimony trioxide has excellent properties, and if a paint manufacturer were limited to a single white pigment, antimony trioxide would probably come closest to being ideal from the stand point of its physical and chemical properties. Its cost, however is gretaer than most other white pigments, and so it is generally used only in certain high quality preparations."[25]

## B. Antimony Trioxide as a Fire-Retarding Chemical

Many plastics, textiles, and paints used, tend to burn when they are subject to flame. Some paints burn even when they are not subject to flame but when the substance on which they are applied is heated to high temperatures. This tendency of these substances, makes a fire more hazardous. But by proper processing they can be rendered less dangereous. This is the point when fire retardation comes into the scene.

The term "fire-retardant" is used to describe materials which may be destroyed by exposure to flame but which do not further the spread of fire[5]. Interest in these materials is wide spread and numerous patents are issued in many countries on this subject. Primary emphasis in fire retarding has been directed to coatings or impregnants which will protect a combustible substrate. High pigment volume and antimony trioxide have been found to achieve fire-retardance, but high pigment volume induces unsatisfactory properties, such as poor resistance to staining and high humidity[5]. When antimony trioxide is used in conjunction with chlorinated materials better fire-retardance is achieved. No satisfactory theory has yet been suggested to explain the synergism between chlorine and antimony compounds in conferring fire-retardance.

Birnbaum and Markowitz[5] performed an experiment in order to determine the effect of antimony trioxide and chlorine on the fire retardant properties of paints. Their experiment was essentially heating a painted steel panel and observing the paint. The panels were heated up to 2000 °F (1093.3 °C). Flame rating was prepared such as; a flame rating of ten indicates that no flame was observed and a flame rating of zero indicates that the flame height was more than six inches. A flame rating of nine which indicates a flash, classifies the paint in question as borderline paint. A summary of their results is presented in Tables 6, 7, and 8.

TABLE 6

EFFECT OF PIGMENT CONCENTRATION ON FIRE-RETARDANCE[5]

| PIGMENT CONC., Vol. % | PIGMENTATION A$^{+}$ | | PIGMENTATION Z$^{++}$ | |
|---|---|---|---|---|
| | Film thickness mils | Flame rating | Film thickness mils | Flame rating |
| 20 | 3.2 | 1 | 3.1 | 1 |
| 40 | 3.2 | 4 | 3.5 | 4 |
| 50 | 3.2 | 10 | ... | ... |
| 60 | 3.3 | 10 | 3.0 | 7 |
| 70 | 3.2 | 10 | 3.2 | 8 |

+ This pigmentation contains 11.7 per cent by weight $Sb_2O_3$.
++ This pigmentation contains no $Sb_2O_3$.

The paints used in the above experiment were prepared in a chlorine-free alkyd resin vehicle.

TABLE 7

EFFECT OF ANTIMONY TRIOXIDE CONCENTRATION ON FIRE-RETARDANCE[5]

| $Sb_2O_3$ CONCN., VOL. % | FILM THICKNESS MILS | FLAME RATING |
|---|---|---|
| 0 | 3.5 | 4 |
| 7.8 | 3.2 | 4 |
| 20 | 3.0 | 9 |
| 40 | 3.1 | 9 |
| 60 | 3.0 | 9 |
| 80 | 3.0 | 9 |
| 100 | 2.9 | 9 |

The paints used in the above experiment contained 40 per cent by volume pigment in a chlorine-free alkyd resin vehicle.

TABLE 8

EFFECT OF CHLORINE CONCENTRATION ON FIRE-RETARDANCE[5]

| | 20 % PIGMENT VOL. | | 30 % PIGMENT VOL. | | 40 % PIGMENT VOL. | |
|---|---|---|---|---|---|---|
| Chlorine concn., Wt. % | Film thickness, mils | Flame rating | Film thickness, mils | Flame rating | Film thickness, mils | Flame rating |
| 0 | 3.3 | 3 | 2.9 | 4 | 3.2 | 4 |
| 10 | 2.9 | 4 | 2.9 | 6 | 3.0 | 9 |
| 20 | 2.9 | 7 | 2.9 | 8 | 3.4 | 9 |
| 30 | 3.1 | 6 | 2.9 | 9 | 3.0 | 10 |
| 40 | 3.2 | 8 | 3.2 | 9 | 3.1 | 10 |
| 50 | 3.5 | 8 | 3.2 | 10 | 3.3 | 10 |
| 60 | 3.1 | 10 | 3.4 | 10 | 3.4 | 10 |
| 70 | 3.5 | 10 | 3.7 | 10 | 3.6 | 10 |

The paints used in the above experiment were prepared in a chlorinated paraffin wax-alkyd resin vehicle, and the pigment contained 7.8 per cent by volume of antimony trioxide.

These experiments conducted by Birnbaum and Markowitz[5] clearly indicate that antimony trioxide and organically combined chlorine are of value as agents to impart fire-retardance.

Textiles, in general, burn when they are subjected to flame and even after the flame is removed the after glow consumes the material. Therefore the textiles, which are to be used in places where there is a danger of fire, should have fire and glow retardant qualities. In general there are two types of fire-retardant finishes for textiles, namely, transient and permanent finishes. The transient fire-retardant qualities of a textile are easily removed when they are leached by rain, water, perspiration, moisture and laundering. The permanent finishes are obtained by depositing insoluble material on the fabric. These deposits are mainly a mixture of fire-retardant salts or oxides, such as $Sb_2O_3$, with a chlorinated paraffin wax vehicle and they are applied on fabrics from their suspensions in a solvent[11].

The following mixtures are reported by Coppick et al[7] to give excellent durable fire-retarding qualities to textiles:

Antimony trioxide - chlorinated paraffin wax - zinc borate, 33 per cent added, laboratory treatment emulsion.

Antimony trioxide - chlorinated paraffin wax - zinc borate, 35 per cent added, commercial treatment emulsion.

Antimony trioxide - polyvinylchloride - zinc borate, 40 per cent added, semicommercial treatment from organic solvent suspension.

Antimony trioxide - zinc chloride - borax, 29 per cent added, commercial treatment, organic solvent double bath.

Treatments with these types of mixtures give the fabric a quality which is called "FWWMR", which is the abbreviation for "fire, water, weather, and mildew resistance". The only disadvantage of these treatments is that it causes an increase in the weight, and a decrease in porosity of the treated fabric[11].

Antimony trioxide has long been used extensively as a fire-retardant additive in polymers. But it is insoluble in most commercial polymers and thus produces opaque compositions. The use of, the diene reaction adduct of hexachlorocyclopentadiene with maleic acid, in the synthesis of polyester resins, produces fire-retardant polyesters, but for good fire-retardance the addition of a small proportion of antimony trioxide is necessary[28].

Polyvinylchloride provides the largest single market for fire-retardant chemicals in the plastic industry[18]. Antimony trioxide, in spite of the disadvantage that opaque compositions result, is the most efficient fire-retardant in this material and about 80 per cent of the antimony trioxide consumed in the plastic industry is used in fire-retardant polyvinylchloride compositions[18]. Fire retardant grades of plastics, such as ploystyrene, and polyolefins, which do not contain chlorine in their compositions, can be prepared by the addition of antimony trioxide in conjunction with chlorinated paraffin waxes[18]. Again the only disadvantage is the formation of opaque compositions.

Consumption of fire retardant chemicals in the United States are listed in Table 9. The table clearly illustrates that the antimony trioxide is, with the exception of phosphate esters, the most widely used fire-retardant chemical in the United States of America.

TABLE 9
CONSUMPTION OF FIRE-RETARDANT CHEMICALS
IN THE UNITED STATES[18]

| MATERIAL | AMOUNT CONSUMED, MILLION LBS. | | | |
|---|---|---|---|---|
| | 1960 | 1963 | 1964 | 1965 |
| Unreactive Types | | | | |
| Phosphate esters | 26 | 31 | 34 | 38 |
| Antimony trioxide | 10 | 15 | 15 | 20 |
| Chlorinated paraffin waxes | 6 | 8 | 7 | 7 |
| Others | 1 | 2 | 2 | 2 |
| Total | 43 | 56 | 58 | 67 |

# IV EXPERIMENTAL

## A. Design of the Apparatus

The production of antimony trioxide from antimony ore by volatilization can be summarized as: heating the ore under a stream of air and collecting the antimony trioxide formed. Therefore the apparatus can be considered in three parts; a) air supplying part, b) reactor, c) collecting part.

### 1. Air Supplying Part

The air was pumped into the reactor by means of a compressor. The compressor used was made by Cenco Scientific Company, and it was designed to work both as a vacuum pump and a compressor. It was equipped with a 1/4 HP electric motor made by General Electric Company. Its output was 1.1 cubic feet (31.2 lts.) air per minute at the maximum, as measured by a wet gas meter. The air supply was regulated by a clamp squeezing the rubber tubing leading to the reactor.

Figure 2: The Air Supplying Part

Since the air supplied was found to cool the reactor in the preliminary runs the air was preheated before entering the reactor. This was accomplished by means of a copper tube of 1/4 inches (0.635 cm.) outer diameter, and about 40 inches (101.5 cm.) long. This tube was bent in the form of a coil and one end was connected to the compressor by means of a rubber tubing and the other end was connected to the air inlet of the reactor again by means of a rubber tubing. The coil was placed on a piece of sheet iron to ensure uniform heating and was heated by means of two bunsen burners. By this set up the air could be heated up to 80 °C which sufficed for our purpose. The final form of the air supplying part is shown in Figure 2 above.

### 2. The Reactor

The functions required from the reactor led us to the conclusion that; the reactor should be a closed vessel except for the three holes, one for the inlet, one for the insertion of the thermocouple and the mixer, and one for the outlet of antimony trioxide fumes. It had to stand up to 500 °C and it should be inert to $Sb_2S_3$ and $Sb_2O_3$. First, an iron vessel was considered but iron is not inert to $Sb_2O_3$ and reacts with it according to the equation:

$$Sb_2S_3 + 2Fe = 2Sb + Fe_2S_3$$

Lining the iron vessel with firebrick introduced some technical hadicaps because of the small size and irregular shape of the reactor considered. Therefore, a three necked pyrex flask was taken as the reactor. The flask chosen was a one liter pyrex flask, the largest available in the laboratory, with a 34/55 ground jointed central neck and with two 24/40 groud jointed side necks.

The flask was heated with an electrical heater, to insure uniform heating and to avoid local overheating in the charge, since it would cause fusion of the ore. The heater chosen was equipped with an iron-constantan thermocouple and the voltage was regulated with a variac. The temperature of the heater was measured with a pyrometer. The maximum permissable operating temperature of the heater was 450° C which was sufficient for our purpose.

The temperature of the charge in the reactor was measured by means of an iron-constantan thermocouple. Since the charge was corrosive to iron, we had to put the thermocouple measuring joint into a pyrex tube, of which one end was sealed. Sand was added into the pyrex tube as packing and to increase the heat transfer rate and consequently the sensitivity of the thermocouple. The thermocouple was connected to a Fisher pyrometer, manufactured for temperature measurements with iron-constantan thermocouples. Studies made on the calibration of the thermocouple revealed that the pyrometer reading was indicating the difference between the measured temperature and the room temperature. Also a study was made to determine the sensitivity of the thermocouple and the pyrometer. In this study the thermocouple was suddenly immersed into boiling water at 100 °C and the pyrometer readings were ploted versus time. The room temperature, at the time of experiment was 18° C as measured with a mercury thermometer.

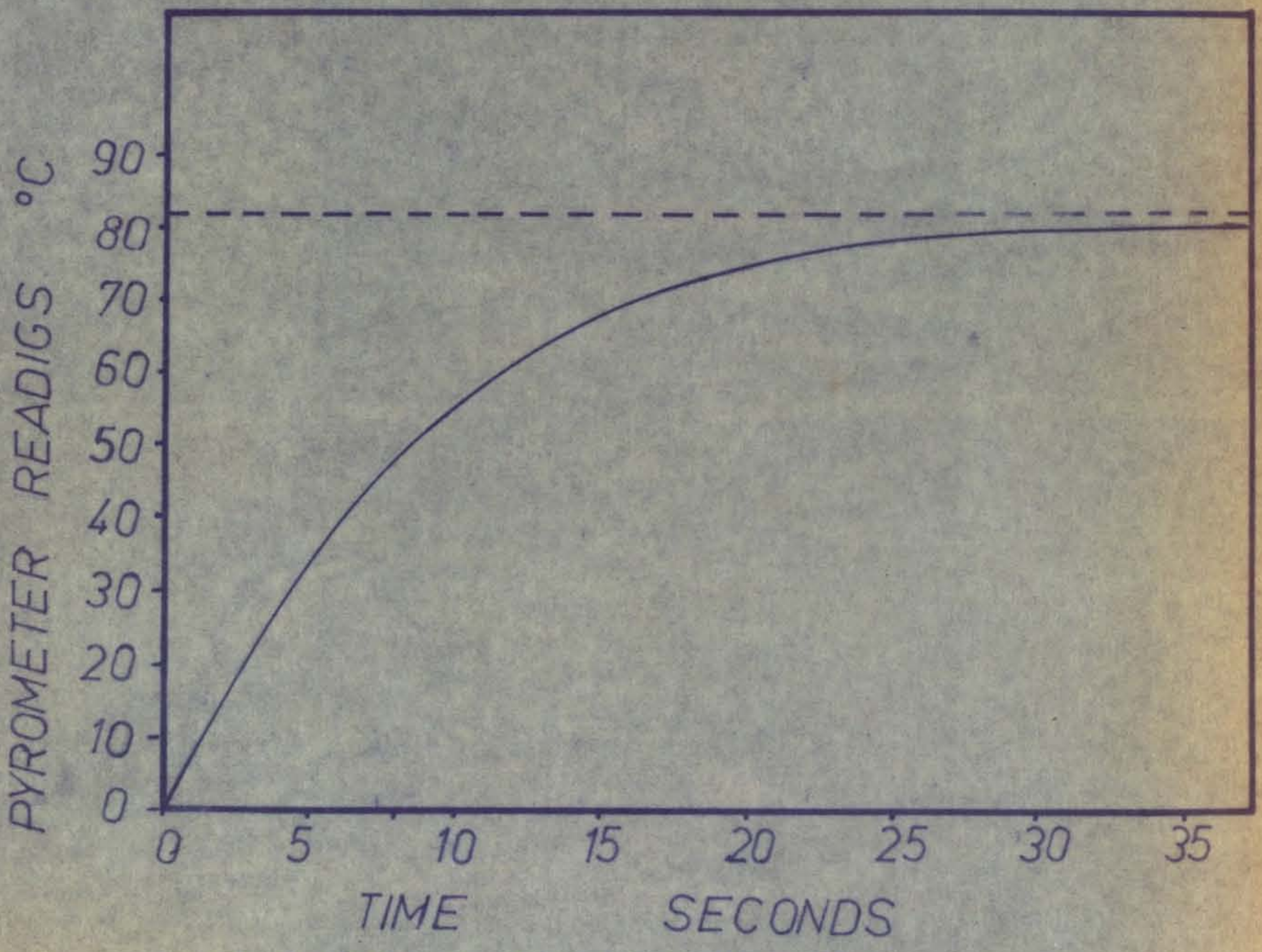

Figure 3: Response of the Thermocouple

This study has shown that the time constant of the thermocouple, which is the time required to reach 63.2 per cent of the final value[12] was 8 seconds. The time required to reach the 98 per cent of the final value was 32 seconds. This sensitivity was sufficient for our purposes.

The reactor was also equipped with a mixer. The mixer was made from a stainless steel wire. This was the best material available, even though the charge was known to be corrosive to steel. But the experiments showed that this corrosion was very small to interfere with the reaction. Both the thermocouple and the mixer were placed into the reactor through the central neck by means of a rubber stopper.

Figure 4: The Reactor

## 3. Collecting Part

The collecting part consisted of a pyrex condenser and a filter bag. This combination was connected to the reactor after the reactor had reached about 320 °C. Before that, a rubber tubing was connected to the reactor, to lead the air mixed with sulfur dioxide gas, which forms from the roasting of antimony sulfide at temperatures higher than 200 °C, out of the reactor. At around 320 °C the rubber tubing was replaced with the condenser and filter bag combination to collect the antimony trioxide which starts to volatilize at about 330 °C.

The condenser was connected to the reactor by means of a ground jointed adapter. The other end of the condenser was connected to the filter bag by means of another ground jointed adapter and a rubber stopper.

The filter bag was prepared from a tightly woven cotton fabric. By trial and error a fabric with 858 wraps and wefts per square centimeter was found to be of optimum efficiency. The filter bag was required to hold all antimony trioxide particles formed and it should not cause a high back pressure. The preliminary experiments have also shown that the color of the fabric was also important. Colored fabrics were found to cause colorization of the product. Therefore a white fabric was chosen for the filter bag.

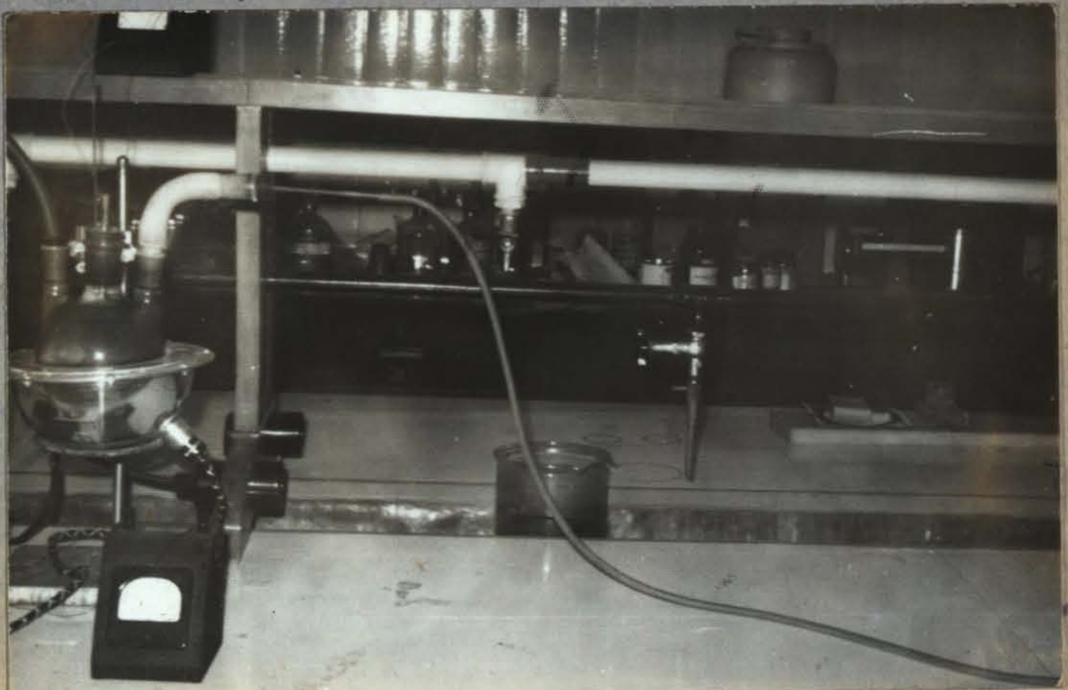

Figure 5: Collecting Part (below 320 °C)

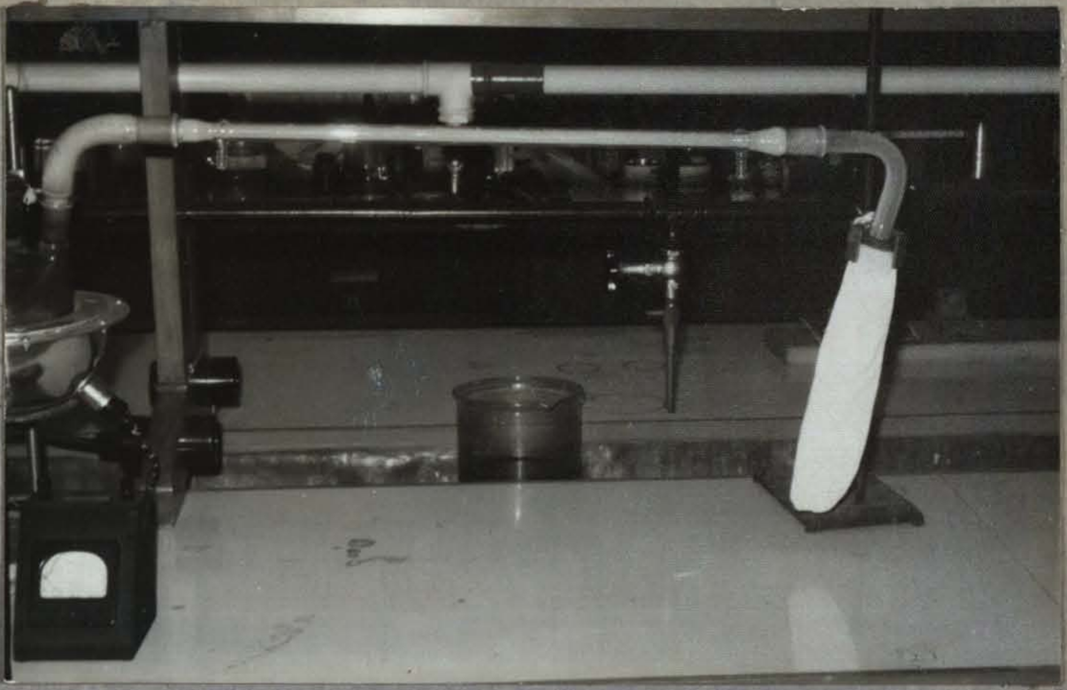

Figure 6: Collecting Part (above 320 °C )

Figure 7: Final Form of the Apparatus

## B. Preliminary Experiments

The original shape of the apparatus did not have the heating coil. The collecting part consisted then of a condenser and a filter bag. The condenser and the filter bag were connected to the reactor from the beginning of the process. By this set up the temperature of the charge could not be raised above 300 °C. Therefore, no product could be obtained. Then, the copper coil was inserted between the compressor and the reactor to preheat the air. By doing this, the temperature of the feed was raised up to 400 °C and a product could be obtained. The product obtained was gray in color. A close observation on the condenser showed that there were small particles of ore and some yellow spots which were condensed sulfur. Even working with highest air rate possible, with the thought to fully oxidize the sulfur and to avoid condensation of partially oxidized sulfur did not improve the stuation. On the contrary, the amount of carried-over ore particles increased. Therefore, the use of a separate outlet until the volatilization temperature of antimony trioxide was reached, was tried. In this trial, a glass tube was connected to the outlet end of the reactor and the out coming gases, which were a mixture of sulfur dioxide, nitrogen and some unreacted oxygen were led out of the laboratory by means of a rubber tube. The air volume was around 1 cubic foot (28.316 lts.) per minute. When 320 °C was reached, the glass tube was replaced by the condenser and filter bag combination. This trial gave a pale ivory product. The impurities collected in the glass tube supported our assumption that, the gray color was due to the contamination of the product by ore particles and condensed sulfur. By this set up the ore particles which could be carried over by the air stream were carried over before the filter bag was connected. Also, the use of the glass tube when the sulfur fumes were more dense, prevented the contamination of the bag before the product was collected. But the analysis of the product showed that the product contained only 58.82 per cent $Sb_2O_3$ and 41.16 per cent $Sb_2O_4$.

The result led us to a study to find the air rate which would give the best product. The air rate was adjusted by means of a screw on the clamp, squeezing the rubber tube, connecting the compressor to the copper coil. At very low air rates, the charge temperature increased too much, even when cold air was blown, and this caused fusion of the charge. Also at this slow air rate the antimony trioxide could not be carried to the bag but it was mostly collected at the outlet end of the reactor. By trial and error the best air rate which gave a product of 99.26 per cent antimony trioxide was set. At this rate a test run was performed to obtain full data on the operating conditions, and numerous runs were made to collect enough product for the determination of the properties of the antimony trioxide produced.

### C. The Procedure and the Results of the Test Run

The apparatus was assembled. To measure the air flow a "Precision Wet Test Meter" produced by Precision Scientific Company was connected to the end of the apparatus. This was done by putting the filter bag into a pyrex suction flask and connecting the outlet of the flask to the gas meter as indicated in Figure 8.

Figure 8: The Connection of the Gas Meter to the Filter Bag

A more accurate result could be obtained by connecting the gas meter between the compressor and the copper coil but the mechanism of the meter was such that; the incoming gas was displacing the water in the meter, causing the rotor turn. Therefore the outcoming gas would be humid and that was undesirable in the reactor.

The ore used in our experiments was obtained from "Özdemir Antimuan Ltd." company and it was a representative sample of the ore which was exported to Czechoslovakia. The ore was reported[26] to contain 60.1 per cent Sb and 0.5 per cent Pb+As. The qualitative analysis made in the laboratory indicated that the ore also contained Fe in it. But, since the quality of the ore is judged by its Sb and As content, the Fe content is usually not determined.

Ten grams of the ore were placed into the reactor through the central neck. Then the thermocouple and the mixer were placed. The bunsen burners heating the copper coil were lighted and the electric heater was turned on. After the pyrometer connected to the thermocouple started to indicate that the charge is warming up, the compressor was started. The set of the clamp on the rubber tube was kept the same as the set determined by trial and error in the preliminary experiments. The air rate was measured by timing the rotation of the pointer on the gas meter by a "Smith" stop-watch. The air rate was found to be 0.21 cubic feet (5.95 lts.) per minute. This timing of the pointer was done throughout the experiment at certain intervals. The air rate was found to stay almost constant. A thermometer was placed near the connections of the pyrometer to determine the room temperature at that point. The room temperature was 23 °C. Therefore, 23 °C had to be added to the pyrometer redaings.

The outlet of the reactor was connected to the gas meter by a glass tube and a rubber tube at this time. When the temperature of the charge reached 223 °C (200+23 °C) the $SO_2$ evolution started. This point is also clearly visible in the temperature versus time plot prepared from measurements done during the experiment as shown in Figure 9. Since the reaction ($Sb_2S_3 + 3O_2 = 2Sb + 3SO_2$) is exothermic, the slope of the curve suddenly changes at this point.

When the temperature of the charge had reached 323 °C (300+23 °C the rubber tube was replaced by the condenser-filter bag combination and the whole set was connected to the gas meter as explained above. At 333 °C (310+23 °C) the $Sb_2O_3$ evolution started. After this point the mixer was operated by hand to break any crusts formed on the charge and thus, to facilitate the evolution of $Sb_2O_3$. When the charge temperature had reached 423° C (400+23° C) the temperature of the heater

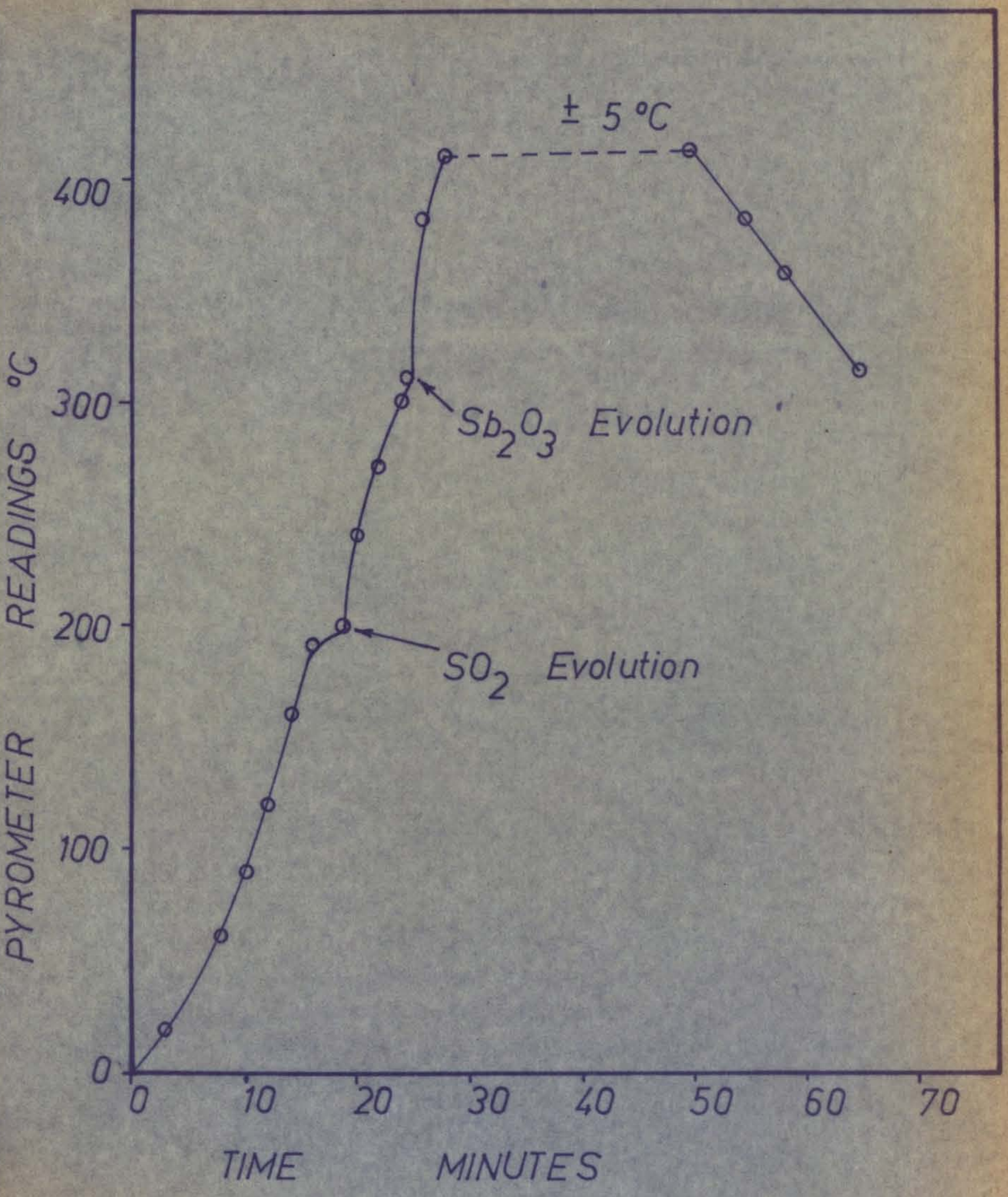

Figure 9: Reactor Temperature Versus Time

was manupulated by means of the powerstat to keep the charge temperature constant around 420° C. This could be accomplished, but small fluctuations of the temperature could not be avoided. But this was not critical. The purpose of this was to prevent the charge to reach temperatures where it would fuse. After 50 minutes of operation, the temperature of the reactor started to decrease. This was due to the decrease in the reaction rate. The reaction was carried on until the temperature had dropped below 330° C.

The results obtained from this run are presented below.

| | | |
|---|---|---|
| Product: | color; White with a slight pale ivory tint. | |
| | composition; 99.26 per cent $Sb_2O_3$ | |
| | 0.73 per cent $Sb_2O_4$ | |
| Yield: | Product obtained in the filter bag: | 5.6 grams |
| | Product remaining in the condenser and the filter bag is estimated to be: | 1.0 grams |
| | Total: | 6.6 grams |
| | Theoretical yield : | 7.2 grams |
| | Percentage yield : | 92 per cent |

## D. Experiments With the Product

### 1. Hiding Power

There is no absolute method for hiding power measurements. Therefore the hiding power of antimony trioxide was determined relative to commercial titanium dioxide (rutile) and high strength lithopone. The method followed was ASTM method D 406-39[1]. Although the essentials of the method were followed, small modifications were made in the details. The test surface was prepared from a photographic smooth-surfaced paper which was printed to have adjacent black and white strips. The photographic paper was chosen because of the impermeability of its surface to paint. The vehicle used was a 1:1 mixture of heat-bodied linseed oil and light, boiled linseed oil. They were obtained from the market under the trade names of "Çavuşoğlu Boya Sanayii Superlux Türk Beziri" and "Çavuşoğlu Boya Sanayii Superlux İngiliz Beziri". To each 100 gram linseed oil mixture used, 1 mililiter of cobalt naphthanate drier (metal content, 8 per cent) was added. The quantities of pigment and vehicle used are the values suggested by the ASTM method and are shown in Table 10.

TABLE 10

QUANTITIES OF PIGMENT AND VEHICLE USED

| PIGMENT | PIGMENT (g.) | OIL FOR MULLING (ml.) | OIL FOR THINING (ml.) |
|---|---|---|---|
| Antimony trioxide | 25.3 | 5.3 | 5.3 |
| Titanium dioxide | 11.6 | 6.6 | 5.6 |
| Lithopone | 13.9 | 3.8 | 8.0 |

The amount of pigment shown in the table was weighed and it was mulled with the respective amount of vehicle indicated in the table on a smooth porcelain slab using a spatula. After a thoroughly homogeneous mixture was obtained the second part of the vehicle was added to obtain a mixture of painting consistency. Then these paints were applied on the previously weighed test surfaces until the black and white strips were no more visible. Then the painted charts were weighed and they were set aside to dry.

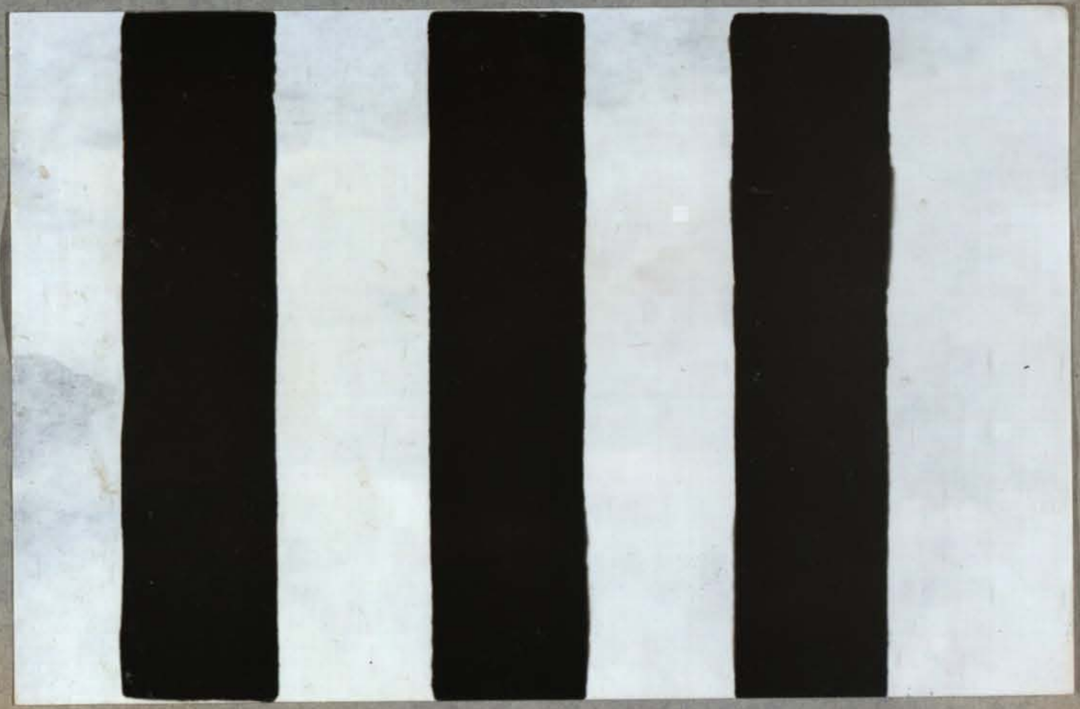

Figure 10: Test Surface Used in Hiding Power Determinations

Upon drying there was a slight decrease in the hiding power of antimony trioxide and lithopone paints, but the hiding power of titanium dioxide paint remained unchanged. Table 11 below, gives the results obtained in this experiment. The specific gravity of the linseed oil mixture was determined by a pycnometer and was found to be: 0.969.

TABLE 11

RELATIVE WET HIDING POWERS OF THE PIGMENTS USED

| | ANTIMONY TRIOXIDE | TITANIUM DIOXIDE | LITHOPONE |
|---|---|---|---|
| Paint applied to the test surfaces (g.) | 5.9690 | 2.5684 | 5.4246 |
| Pigment content of the paint, % by weight | 63.9 | 49.5 | 54.9 |
| Amount of pigment applied | 3.8142 | 1.2714 | 2.9781 |
| Relative wet hiding powers | 33.3 | 100.0 | 42.8 |

## 2. Oil Absorption

The method followed was ASTM method D 281-31[2]. The oil used was the same mixture of linseed oil used for hiding power determination. A weighed amount of pigment was placed on a porcelain slab. The oil was added gradually to the pigment drop by drop from a burette. After the addition of each drop the oil was thoroughly incorporated with the pigment by rubbing up with a spatula. The test was completed when enough oil has been incorporated with the pigment to produce a very stiff, putty-like paste, which does not break or seperate. The oil consumed was recorded and the results were calculated as the pounds of oil required to wet 100 pounds of pigment. Table 12 shows the results obtained for the three pigments tested.

TABLE 12

OIL ABSORPTION OF PIGMENTS

| PIGMENT | OIL ABSORPTION lb. oil/100 lb. pigment |
|---|---|
| Antimony trioxide | 19.8 |
| Titanium dioxide | 51.7 |
| Lithopone | 25.9 |

### 3. Hydrogen Ion Concentration (pH Value)

A five per cent by weight suspension of the pigment in water was prepared. The suspension was throughly mixed with a magnetic stirrer and the pH was measured by means of a "Beckman Zeromatic pH Meter". The pH value of the five per cent by weight suspension of antimony trioxide in water was: 5.2

### 4. Matter Soluble in Water

The method followed was ASTM testing method D 1208-52T[3]. Ten grams of antimony trioxide were weighted accurately and placed in a 400 mililiter beaker. A hundred mililiters of water were added, boiled for five minutes, cooled and transferred to a 250 mililiter volumetric flask quantitatively. They were diluted to 250 mililiters, mixed and were allowed to settle. The supernatant liquid was filtered into a previously weighted beaker. A hundered mililiters of the filtrate were collected and then the filtrate was evaporated to dryness. The beaker was again weighted and the weight of the residue was determined. The ammount of matter soluble in water was 0.39 per cent.

### 5. Fire-Retardant Polyvinylchloride

The polyvinylchloride was prepared according to the laboratory procedure, used in the industrial chemistry laboratory. According to this procedure; a paste consisting of 100 parts (all by weight) of fine powdered PVC and 40 parts of dioctyl phthalate is homogenized by thourough mixing. A second mixture is prepared by fine grinding of 20 parts of barytes, 8 parts of white lead, and 1 part of a pigment in a mortar and homogenizing it in 40 parts of dioctyl phthalate. Both mixtures are intimately mixed together. This mixture is then poured on glass and is baked at 150-180° C for five minutes. For the fire-retardant PVC, instead of 20 parts of barytes, 12 parts of barytes and 8 parts of antimony trioxide were added.

TABLE 13

COMPOSITION OF THE FINAL PASTE (NORMAL)

| ADMIXTURE | FUNCTION | PARTS BY WEIGHT | PER CENT |
|---|---|---|---|
| PVC | Paste making powder | 100 | 47.85 |
| DOP | Plasticiser | 80 | 38.28 |
| Barytes | Filler | 20 | 9.57 |
| White lead $(Pb_3(OH)_2(CO_2)_2)$ | Heat stabilizer | 8 | 3.82 |
| Pigment | Pigment | 1 | 0.48 |

TABLE 14

COMPOSITION OF THE FINAL PASTE (FIRE-RETARDANT)

| ADMIXTURE | FUNCTION | PARTS BY WEIGHT | PER CENT |
|---|---|---|---|
| PVC | Paste making powder | 100 | 47.85 |
| DOP | Plasticiser | 80 | 38.28 |
| Barytes | Filler | 12 | 5.75 |
| Antimony trioxide | Fire-retardant chemical | 8 | 3.82 |
| White lead $(Pb_3(OH)_2(CO_2)_2)$ | Heat stabilizer | 8 | 3.82 |
| Pigment | Pigment | 1 | 0.48 |

A piece of each product was taken to test for their fire-retardant properties. They were fastened to an iron stand by two pieces of wire. Then they were exposed to the flames of two bunsen burners. Both started to burn. As soon as the bunsen burners were taken away, the one containing antimony trioxide stopped burning, whereas the other one continued burning until it was extinguished.

Figure 11: The Two Pieces of PVC, When Exposed to Flame

Figure 12: The Two Pieces of PVC, Right After the Flame is Removed

## 6. Analytical Methods

The composition of the product, indicated in parts 3 and 4 were found by following the procedures given in "Bureau of Mines and Geology Pamphlet No.89"[25].

a. Determination of $Sb_2O_3$. Weigh accurately 0.15 to 0.20 grams of the oxide. Add 5-10 mililiters concentrated HCl and warm until all the oxide dissolves. Add approximately 3 grams of tartaric acid and dilute to about 50 mililiters. Make the solution basic to phenolphthalein with a saturated solution of $Na_2CO_3$. The solution is then made barely acidic, and approximately 30 mililiters of cold saturated solution of $NaHCO_3$ (or 2 grams of the salt) are added. Starch indicator is added and the solution is titrated with a standard iodine solution.

b. Determination of $Sb_2O_4$. Dissolve a 2.0 gram sample of the oxide in dilute HCl (one volume of strong acid in three volumes of water). Add 1 gram of KI; add starch solution and titrate with standard $Na_3S_2O_3$ solution.

# V. DISCUSSION

## A. Discussion of the Method

The method of producing antimony trioxide by volatilization process may seem to be a slow process if it is compared with other methods of producing antimony trioxide, such as; volatilization of antimony trioxide by blowing air into molten antimony[25]. Actually, the process is not a slow one if we think of the production in terms of time required to convert the ore into antimony trioxide. Because production of the antimony from the ore and volatilization of the antimony trioxide from the molten antimony is a more labor and time consuming process than the production of antimony trioxide directly from the ore. Besides, the process of obtaining antimony trioxide from molten antimony, requires temperatures higher than 1000° C[25]. This of course will require an equipment which can stand high temperatures and consequently the investment for equipment will be higher.

The volatilization process requires higher air volumes than that theoretically required. This is necessary in order to keep the temperature of the charge below the fusion temperature of the ore. But, this will increase the $Sb_2O_4$ content of the ore, unless the air volume is carefully regulated. Also care should be taken to insure complete oxidation of the sulfur to sulfur dioxide, in order to avoid contamination due to condensation of partially oxidized sulfur. Further, when finely ground ore is used, measures have to be taken, so that ore particles are not carried over by the air stream.

The collection of the product can be done by using any suitable gas-solid separator. In the case of antimony trioxide the particle size is very small. Therefore, settling chambers and cyclone separators cannot be used. Cottrell precipitators have been found to be very efficient, but cheaper methods such as filter bags, can also be used with reasonable efficiency.

As a result, this process can be used for the production of antimony trioxide, provided that the process variables are carefully controlled. The equipment will be cheaper than the equipment which will be required by the other process. It has another advantage that, very low grade ores which can hardly find a market can be utilized by this process. These ores which do not have an economic significance today can be evaluated by this process, and since they can be obtained with a low price, the raw material costs will be reduced.

## B. Discussion of the Apparatus

The apparatus used for our study enabled us to regulate the process variables easily. This flexibility of the variables, such as air rate and temperature, was very important for our purposes. Becauee, our aim was to find the optimum values for the air rate and temperature which will yield the best product which can be obtained from such a process. The electric heater used was very suitable becauee a uniform and controlled heat was obtained. But a heater with a higher heat output would be more suitable. This would eliminate the need for the preheater. The shape of the reactor was not the most suitable shape for the process. A reactor with a greater cross section, which would make charging greater amount of material with a small depth possible, would be more suitable. The great contact area of the charge with air in this type of a reactor will increase the reaction rate. But since our aim was to show that antimony trioxide can be produced from local ores under controlled conditions, this defect of the reactor did not make an effect on our studies.

The collecting part was sufficient. The condenser and the bag functioned efficiently through out the process. Although the material used for the filter bag was found to be sufficient during our experiments, a further study can be made on the choice of the material. The fabric should not loose its strength at the operating temperatures, it should be inert to the product and its texture should not be too loose or too tight. A loose texture would allow the product to escape and a tight texture would increase the back pressure and consequently the load of the compressor would increase. With a more thorough research in the market a fabric which complies with this requirements better than the one we used may be found. As for the shape of the bag; our bag was sufficient for small quantities of product. When larger quantities of product are expected, a hopper shall be fitted to the bottom of the bag and the bag should be shaken at intervals to cause the product to fall into the hopper. Because, as the layer of the collected product becomes thicker, the back pressure caused by the bag becomes greater and at some point the bag does not let the air pass through, and this causes the reaction to stop.

## C. Discussion of the Results

The total test time of the test run was 65 minutes but the reaction time was 40 minutes, because, the antimony trioxide evolution has started at the 25th minute. The yield obtained in this time interval was found to be 6.6 grams. Therefore the reaction rate was 0.165 grams of antimony trioxide per minute. This reaction rate is low, but the reaction rate is proportional to the contact area of the charge with air. Considering that the surface area of the charge in our reactor was small, the reaction rate is not as small as it seems.

The product obtained, composition wise, was of high quality but the snow white color of antimony trioxide could not be obtained. Our product had a slight pale ivory tint. Newton et al[25] explain the tint in their oxides as due to incomplete crystallization of antimony tetraoxide at low fume temperatures. And they report that this disappeared when the fume temperature was high, because the complete crystallization of antimony tetraoxide was possible at high temperatures. The reason for the slight pale ivory tint in our product was most probably this phenomenon. Our operating conditions restricted the temperature to below 450°C and therefore this tint could not be eliminated. Actually, in the literature there are notes indicating that antimony trioxide of pure white color cannot be obtained by volatilization from the ore. This defect of the product is only significant when the pure white color of the pigment is the major requirement. The pigment obtained by this process can be used in all colored paints as an opacifier, chalking resistant filler, and for the improvement of hiding power. It can also be used in colored enamels and lacquers.

The test done in order to determine the fire-retarding properties of this pigment was succesful. The fire-retardant polyvinylchloride composition prepared had no after flaming and no after glow. Considering that the quantity of antimony trioxide used was only, 8 parts by weight per 100 parts of polyvinylchloride, it is obviously that this pigment has a great value as a fire retardant in chlorine containing substances. Actually the fire-retarding properties of antimony trioxide, together with chlorinated paraffin waxes, are experimentally verified facts as discussed in capter III-B. Our pupose in doing this test was only to show that also antimony trioxide obtained by volatilization process has the fire-reatarding properties.

The wet hiding power of antimony trioxide was found to be 30 per cent of the wet hiding power of titanium dioxide and 78 per cent of the wet hiding power of high strength lithopone. These two pigments are among the pigments which have very high hiding powers. Especially titanium dioxide has the highest hiding power as shown in Table 3. Therefore these results should not mislead the reader to the conclusion that antimony trioxide has a low hiding power. Actually it has an intermediate hiding power when all white pigments in the market are considered. The dry hiding powers of the pigments tested, could not be determined. The paints on the test surfaces were wrinkled when they were dry. This was partly due to the fact that the paint film applied was very thick. The other reason was probably due to the nonconformity of the linseed oil and the drier used. But the linseed oils used were the best ones available in the market and the cobalt naphthanate drier was used in order to follow the procedure given in the ASTM method. In order to check this possible nonconformity, a film of linseed oil and drier mixture was applied on a test surface. When it dried this film wrinkled. Thus, it was concluded that there was a nonconformity between the linseed oil and the drier used. But no further study was made on this subject, because the wet hiding power is a sufficient measure of the hiding power of a pigment.

The oil absorption test showed that antimony trioxide needs only a small quantity of vehicle in order to form a paste of painting consistancy. This is an advantage of this pigment because it means that paints with very high pigment content can be prepared with this pigment.

From the experiments conducted, in order to determine the properties of antimony trioxide produced by volatilization of local ores, it can be concluded that, the product obtained in the laboratory has the same properties as the antimony trioxide used throughout the world. The only difference is in the color of the product but this is not very significant when the pigment is used for purposes which do not require a pure white color.

## VI. CONCLUSION

The properties of antimony trioxide were known to ones interested in this subject. Our study confirmed the fact that pigment grade antimony trioxide can be produced by volatilization from its ores provided that the process variables are carefully controlled. This has been done by making use of Turkish ores which also confirmed that the process can be successful when local ores are used. The results of this study, however, can not be generalized, that is, if such a process is going to be used in the production of antimony trioxide, these results cannot be used as a base for the design of the equipment. The shape and the size of the equipment has an effect on one of the main variables, that is the air rate, and this has to be determined for the equipment in question. Our aim was to determine whether such a process can be utilized and our studies have proved that under regulated conditions this process can be successful.

The color of the product, however, was not suitable for purposes where the major requirement is the whiteness of the pigment. But the use of white pigments is not only to give white color. They are also widely used for the improvement of hiding power, as opacifiers, and as fillers. Our product has the same qualities as the pure white colored antimony trioxide produced by other processes, for the above mentioned purposes. Besides antimony trioxide has fire-retarding properties, which no other white pigment in the market posesses. Thus, antimony trioxide, will fulfill two functions for fire-retardant paints. It will both function as a pigment and as a fire-retarding chemical. This fire-retarding property alone is sufficient to provide a large market for antimony trioxide. This is apparent from the consumption of antimony trioxide as a fire-retarding chemical in the United States, which was 20 million pounds in 1965, as shown in Table 9.

Antimony ore production of Turkey in 1968 was 2290 tons of ore containing approximately 50 per cent antimony. Assuming 90 per cent yield, this ore would give about 1200 tons of antimony trioxide. If the low grade ore, which is not mined today, is utilized, this figure can go up to 2000 tons of antimony trioxide per year.

For an exact price estimation, the capacity of the plant, the quantity of low grade ore which is going to be utilized, the site of the plant, the equipment, and the fuel which will be used heve to be known. This requires the design of such a plant which is out of our scope. But a rough price estimation can be made. The price of antimony trioxide in the United States was 968 dolars per short ton in 1966[24]. If we assume that our product will cost as much as it costs in the United States, its price will be 9.60 T.L. per kilogram. As a check we calculate the cost of ore per kilogram of antimony trioxide. The Turkish ore containing approximately 50 per cent antimony, costs 2440 T.L. per ton[31]. Assuming 90 per cent yield, antimony ore cost per one kilogram antimony trioxide will be 4.18 T.L. Remembering that, antimony ore is the major raw material required for the production of antimony trioxide, our estimated price of 9.60 T.L. per kilogram which is 2.3 times as much as the ore cost seems reasonable. Titanium dioxide which is the only competitive pigment with antimony trioxide, costs 20 T.L. per kilogram and in addition there is a shortage of titanium dioxide in the market. Thus, it can be concluded that antimony trioxide will easily find its place in the market. Even if it cannot compete with titanium dioxide in the pigment market, it will be consumed as a fire-retarding chemical by the plastic, textile, and paint industries.

This study leads us to the conclusion that; it is worthwhile to build an antimony trioxide plant in Turkey. Such a plant will cause a saving in foreign currency and it will be advantageous to the domestic economy by utilizing the low grade antimony ores which are not mined because there is no market for them.

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