BENEFICIATION FROM TURKISH ANTIMONY ORES FOR IMPORTANT INDUSTRIAL ANTIMONIAL COMPOUNDS

by

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ABSTRACT

A comprehensive literature survey on the production and concentration of the antimonial ore stibnite in Turkey has been done. Methods and ways of beneficiation from stibnite ores and concentrates to produce crudum, antimony trioxides, antimony trisulfides, antimony pentasulfide, antimony trichloride, lead antimonate and metallic antimony have been reviewed. Possible uses of these compounds as pigments fire retarding additives catalysts as major antimonial chemicals of various industries have been investigated.

Practical laboratory set-ups have been devised to produce antimony trioxide and antimony trichloride. Antimony trioxide has been tried to be produced through oxidation and volatilization of stibnite ores and concentrates and of metallic antimony and by hydrolysis of antimony trichloride.

TÜRK ANTİMUAN CEVHERLERİNDEN ÖNEMLİ SINAİ ANTİMUANLI BİLEŞİKLER ELDESİNDE YARARLANILMASI

ÖZET

Antimuan cevheri stibnitin Türkiyedeki üretimi ve zenginleştirilmesi hakkında kapsamlı bir literatür araştırması yapıldı. Stibnit cevherlerinden "credum", antimuan trioksitler, antimuan trisülfitler, antimuan pentasülfit, antimuan triklorür, kurşun antimuanat ve metallik antimuan üreterek yararlanabilme metod ve yolları gözden geçirildi. Bu bileşiklerin pigman yangın geciktirici katkı maddesi ve katalist şeklinde önemli sinai antimuanlı kimyasal maddeler olarak kullanımları incelendi.

Antimuan trioksit ve antimuan triklorürün laboratuarda pratik şekilde eldesi için aletler dizisi kuruldu. Antimuan trioksit'in stibnit cevher ve konsantrelerinden, metalik antimuandan oksitleme ve uçurtma yöntemi ile, ve antimuan triklorürün hidrolizi ile elde edilmesi denendi.

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LIST OF SYMBOLS

M	Lorentz-Lorentz coefficient.
d_{optim}	Optimum diameter.
n_b	Index of refraction of binder.
n_p	Index of refraction of pigment.
λ_i	Wavelength of an emission line.

I. INTRODUCTION

This work reports a study of antimony, antimony oxides and related antimony compounds in respects of literature, their uses and the few experiments conducted in the laboratory. The main object of the task is the determination of a practical method of manufacture of antimony trioxide in view of the demand of this compound in Turkey and to investigate the possible use of this compound as an alternate to other chemicals. Turkey is a producer of the antimony bearing ore stibnite but there are no installations which produce antimony trioxide or other antimonious chemicals of required qualities.

At the start of the work, it was thought that there would be a good outlet of antimony trioxide, besides others, in the pigment market. Of the other white pigments, titanium dioxide is imported at an annual rate of two thousand tons. Contrary to the abundance of stibnite in Turkey ilmenite (the ore of titanium) in rare and beneficiation of titanium from the poor deposite is not economical.

Antimony trioxide has other uses too. Presently this material is imported into Turkey mainly for the use as a catalyst. There are some other major uses such as fire retarding applications not frequent in Turkey. Antimony trioxide can also be used as a starting material in the manufacture of other antimony bearing compounds.

There are different ways of producing antimony trioxide. The easiest in by roasting stibnite in the presence of hot air and separating the volatilized antimony trioxide formed. Antimony trioxide can also be made from metallic antimony by blowing hot air onto the molten metal. Research is going on in many countries for production of this material by other means. Presently air oxidation of stibnite in the most common and economic method practiced by the major producers of the world. The successful oxidation of stibnite to antimony trioxide requires careful control of air flowrate and temperature, since excess air and high temperatures form higher oxides of antimony which are undesirable. There are also various ways of oxidation of stibnite differing mainly in the apparatus employed.

Antimony trioxide can also be produced by hydrolyzing antimony trichloride which can also be obtained from stibnite.

The antimony trioxide produced can be used in production of antimony trisulfides which can also be used as pigment or in pyrotechnics, or again other antimony bearing compounds.

Thinking of the diverse applications of the antimonial chemicals, different laboratory setups have been made to obtain antimony trichloride and antimony trioxide from metallic antimony or stibnite ore and its concentrates. In the production of antimony trioxide from stibnite by oxidation, the object has been to devise a setup which produces a pigment quality product at lowest possible temperatures.

II. LITERATURE SURVEY

A. ANTIMONY ORES AND METHODS OF BENEFICATION

1. History and Geology

Antimony is an element whose compounds have been known since ancient days. There are archeological indications of the use of antimonial materials by Sumerians, early Egyptians, Chinese and Japanese. Antimony has also been encountered as an alloying element in bronze articles of these early civilications (Mellor, 1957). Today more than half of the primary antimony produced every year is used in the form of compounds - mainly trioxide (Joseph, 1977). The rest and the recycled antimony is chiefly used as hardening components of various alloys (Carapella, 1967).

There are many kinds of antimony bearing minerals, the main ones being: Stibnite, Metastibnite (Sb_2S_3), Jamesonite ($Pb_2Sb_2S_5$), Livingstonite ($HgSb_4S_7$), Kermesite (Sb_2S_2O or $2Sb_2S_3.Sb_2O_3$), Berthierite ($FeS.Sb_2S_3$), Alemontite (AsSb), Senarmonite, Valentinite (Sb_2O_3), Cervantite (Sb_2O_4), Stibiconite ($Sb_2O_4.H_2O$). Other known minerals are Schneebergite, Lewisite, Manzelite, Monimolite, Hydromeite, Bindheimite, Stibotantallite, etc. containing elements like Ca, Na, Fe, Ti, Pb, Y, Mn, Ni, Cu, Au, Ag. A good list, about 70 of which are found in Mineral Tables (Dietrich, 1969). Some of these minerals are usually mined for the other elements they include while antimony stands as a byproduct. Antimony itself is very rarely encountered alone in metallic form in nature (Türkiye Antimon Envanteri, 1979).

Antimony mineral beds are found usually in particular geological formations. They are found in small, discontinuous, and disordered masses practically always in the form of lodes or fissure veins, limited in strike and depth and generally of irregular width from a few cm to about 1.5m. They are generally of mesothermal and epithermal origin (i.e. medium to low temperature) having been transported away from the source of magmas molten in carbonates or hydroxides usually in the form of complex sulfides. During cooling the antimonial minerals are supposedly precipitated or solified later so that they are found in the upper parts of the veins thus enabling easy mining. Consequently the antimonial minerals contain other low temperature minerals including As, Hg, Pb, Cu and Ni. Since some of these minerals and associated sulfide ores have good solubility for Ag and Au, these precious metals are also sometimes found in association with antimony (Joseph, 1977; Antimon, 1979).

2. Distribution and Production of Ores in the World

The main antimony-bering ore regions of the world can be grouped into the following metallogenic provinces (Joseph, 1977).

1. Circum Pacific; China, Bolivia, Peru, Honduras, Mexico, North America, Eastern Australia, Thailand, Burma, Japan.

2. Circum Mediterranean: Marocco - Algeria, Spain, France, Italy, Yugoslavia, Greece, Turkey.

3. South Africa.

4. USSR.

The distribution of antimony reserves in the world is given in Table 1.

TABLE 1 - World Antimony Reserves

Total reserves in metal equivalent are estimated to be 4.000.000 tons

Country	Tons
China	2.000.000
Bolivia	400.000
South Africa	250.000
USSR	250.000
Mexico	200.000
Turkey	125.000
Australia	100.000
Yugoslavia	100.000
Thailand	100.000
Sum.	3.525.000

(U.S. Bureau of Mines, 1975)

The annual rate at which antimony is produced and marketed by producer countries are as in Table 2.

TABLE 2 - Average Mine Production of Antimony

Country	Metric tons
China	13.000
South Africa	15.000-19.000
Bolivia	15.000
USSR	8.000
Thailand, Turkey, Yugoslavia, Mexico	3.000-4.000
Italy	1.000-2.000

(Weissler, 1973)

The list in Table 2 can go as low as 6-12 tons in Japan and Korea. There are about 25 countries which manufacture metallic antimony. The rate at which metallic antimony is produced is about the same as that consumed.

Turkey is one of the major producers of antimony bearing ores. It has about 3 percent of the antimony ores produced in the world (Antimuan, 1979).

3. Distribution of ores in Turkey

According to research done by Maden Tetkik Arama Enstitüsü in Turkey, there are about 68 locations where antimony bearing ores are encountered. 10% of these locations are known not to be of economic importance. Most of the remaining require detailed study on the quantity and quality of antimony contained.

The regions which are promising in antimony content are listed in Table 3.

TABLE 3 - Important Antimony Reserves of Turkey

1. BALIKESİR-İVRİNDİĞİ REGION

Location	Activity	Quality and Quantity
Gözlüçayır Çakmakdere	in op$^{\underline{n}}$ since 1970	possibly 9850 tons 39%Sb
Gözlüçayır Ayrıklı-Bağüstü	mine in op$^{\underline{n}}$	20 tons
Gözlüçayır Mındık tarla	mine in op$^{\underline{n}}$	3250 tons
Gözlüçayır Aydınbacılar		2580 tons
Küçükyenice Mezaryanı	mine in op$^{\underline{n}}$	69800 tons
Yaylakıran Kocaburun	operated by a firm	5700 tons
Taşdibi İnekölen	have been in op$^{\underline{n}}$	possibly 47850 tons 6% up to 235000 tons

2. NİĞDE - MERKEZ

Location	Activity	Quality and Quantity
Gümüşler Armutlar tepesi	(not consistently (active but operated (by Rasih and İhsan	2% WO_3, 1% Hg, 4-5% Sb
Gümüşler Örendere		possibly 100000 tons

3. NİĞDE - ÇAMARDI

Location	Activity	Quality and Quantity
Celaller - Kuruçay	not in operation	needs further study
Dedeman	not in operation	average 2-5% Sb, chosen samples 6.4-14.7% Sb
Madsan	in op$^{\underline{n}}$ by Madsan Works	"

4. TOKAT - TURHAL

Location	Activity	Quality and Quantity
Aşağı Geyran	(in operation by	average 11-13% Sb
Yukarı Geyran	(Özdemir Ltd. since	possibly 124000 tons
Elalmış	(1933	

(Türkiye Antimon Envanteri, 1979)

It should be reported that all of the search done by MTA has been concentrated in the western or middle sections of Anatolia. There has been no search for the proof of the existance of antimony bearing ores on eastern Anatolia where volcanic activity has been frequent. It should also be noted that at the eastern border of Turkey and between this boarder and the Caspian sea there are two locations, Nakhichevan and Kağızman of importance. Keeping these in mind, the total antimony reserves of Turkey could be higher than what is estimated.

4. Methods of Ore Treatment

The sulfide of antimony, stibnite (Sb_2S_3), is the only ore of this metal found in sufficient abundance to be of economic consideration, and therefore forms the chief and most common source of antimony metal or antimonial compounds of commerce. The ultimate goal of the early processes have mostly been the isolation of pure antimony in the form of metal. Later stibnite ores started to be treated for antimonial compounds directly.

The ways which stibnite ores are treated can be classified under two seperate headings namely Pyrometallurgical and Hydrometallurgical methods. Pyrometallurgical methods are most common and are well established. Hydrometallurgical methods are commercially successful in only a few cases and are relatively newer. Today before ores undergo these processes they are most always concentrated by flotation.

a) Flotation Technique of Concentration

The practice of flotation technique of concentration on stibnite ores dates as early as 1924 when Parsons had successfully concentrated Lake George (Canada) stibnite ore by flotation, using an added mixture of 40% coal tar and 60% coal tar creosote and 2.3 lb H_2SO_4 for every ton of ore. Later to concentrate the ores, jigs, tables, crushers were added to the flotation cells (Bannister, 1945). Concentration by flotation is achieved by the different "wettability" of constituents in the finely ground ore/matte pulp produced by the addition of specific reagents. When the pulp is agitated and air is finely dispersed in the flotation cells, "wetted" gangue and impurity particles sink and are discarded as tailings, while valuable particles rendered hydrophobous, by organic compounds called promoters, are collected in a froth as concentrate. With the use of this technique recoveries of 90% or more are possible.

Typical reagents used are:

Frothers: methyl isobutyl carbinol, cresylic acid, or pine oil 25 g/ton,

Promoters: Na ethyl xanthate, Na butyl xanthate, K amyl xanthate 25 g/ton,

Modifier: Pb nitrate 1 kg/ton,

Gangue and impurity depressents:pH of 7.5 to 8 is maintained by addition of soda ash, and Na silicate (20 g/ton), NaCN 25 g/ton.

A typical stibnite concentrate has the following composition:

Sb	55-65%	
S	22-26%	
Pb	0.2-1%	
As	0.3-1%	(Joseph, 1977)

b) Pyrometallurgical Methods

Pyrometallurgical methods basically cover the older liquation type of concentration, precipitation methods, blast furnace smelting, oxide volatilization and oxide reduction to obtain metallic antimony.

Liquation involves the moderate heating of the crude ore to melt the sulfide and separate from gangue. The differences in the methods of liquation is based upon the type of furnace used. The oldest (known) method was known to be practiced in the first half of the 19th century in central Europe, involving heating of the crude in a crucible with a hole in the bottom opening into a smaller one below embedded in the ground. A combination of these pots were employed in a circle around a fire all enclosed in a furnace. Later more efficient methods of liquation were developed particularly in France. The first of these were reverbatory furnaces (wind and flame furnaces) where a horizontal flame was used to heat the ore on a concave hearth with a hole in the bottom to collect the product. Later furnaces housing vertical retorts (instead of older crucibles) were used to separate the molten sulfide. Furnaces for continuous liquation were also developed. Liquation has been used to treat ores containing 40-90% stibnite. Ores containing higher stibnites were directly used in later treatments. The residue of these processes contained 12-30% of antimony which had to be recovered using oxidation to volatile trioxide technique (Muspratt, 1860 ; Hunt, 1875; Joseph, 1977; Bannister, 1945; Carparella, 1981).

Precipitation Method. Ores containing over 90% stibnite or liquation products can be reduced to antimony metal by iron precipitation method. Essentially scrap iron is added on molten stibnite to remove the sulfur from antimony and form iron sulphides. Sodium sulphate and carbon are added to enhance separation of the molten antimony and iron sulfide. If not purified the product of this operation is usually contaminated with iron and can only be used in alloys containing iron. The essential reaction is $Sb_2S_3 + 3Fe \rightarrow 2Sb + 3FeS$.

Blast furnace smelting consumes intermediate (25-40 percent) grades of oxides or sulfides or their mixtures to produce metallic antimony. No iron is used in this reduction. The following reactions are claimed to take place:

$$2Sb_2S_3 + 9O_2 \rightarrow Sb_4O_6 + 6SO_2$$

where Sb_4O_6 is antimony trioxide in vapour phase

$$Sb_4O_6 + Sb_2S_3 \rightarrow 6Sb + 3SO_2$$

Air should be present to the extent of allowing the formation of trioxides but not tetroxides of antimony.

Oxide volatilization involves the removal of antimony from the ore as the volatilized trioxide. The collected trioxide is later reduced with charcoal in a reverbatory furnace. This process was proposed by Bobierre, Ruobz and Rousseau in 1844 and was applied later by others most famous of which were Herrenschmidt and Chatillon. The basic advantages of this process is that the poor ores and residues of other processes can be treated with maximum recovery of antimony with least contamination, particularly in arsenic. Many processes have later been developed employing this technique. Oxide volatilization later became the principal method of antimony trioxide manufacture.

c) Hydrometallurgical Methods

This technique employs the selective dissolution of stibnite or other antimony minerals into a liquid solvent. The processes differ mainly by the type of solvent used and by the way which antimony is seperated from this solution. Typical solvents are hot or cold hydrochloric acid, alkali sulfides and ammonium sulfides, alkali or ferric chlorides. Alkali sulfides, hydrosulfides and polysulfides are the most successful.

The following reactions are proposed to explain the dissolution with hydrosulfides

$$3Sb_2S_3 + 6NaHS \rightarrow 6NaSbS_2 + 3H_2S \quad \text{(Mellor, 1957)}$$

with alkali sulfides

$$Sb_2S_3 + 3Na_2S \rightarrow 2Na_2SbS_3 \quad \text{(Joseph, 1977)}$$

with polysulfides : ($2Na_2S + S_2 \rightarrow 2Na_2S_2$)

$Sb_2S_3 + 2Na_2S_2 \rightarrow Na_4Sb_2S_7$

$Na_4Sb_2S_7 + Na_2S \rightarrow 2Na_3SbS_4$ (Mellor, 1957)

The filtered leach solution is later electrolyzed in diaphram cells to obtain 93-99% pure antimony. These processes are also known by other names such as hydrometallurgical and electrowinning methods, recovery by leaching and electrolysis. Another process where antimony can be obtained from the filtered leach solution is known as extraction by lixiviation followed by sodium amalgam reduction. Here the leached solution (sodium thioantimoniate) is introduced under pressure from the bottom into a vertical reaction tube containing an amalgam of sodium (0.2 to 0.5% Na). This precipitates the antimony in the form of a fine powder, while at the same time a sodium sulfide solution is also produced from which filtration seperates antimony (Simons, 1967).

Other methods are still being developed. One interesting method user HCl or Cl_2 gas to treat stibnite to form antimony trichloride and hydrogen sulfide gas. Antimony trichloride can be seperated from the ore in liquid state and be purified by distillation or hydrolyzed to antimony trioxide (U.S. Pat. 3 944 653, 1976).

5. Works Dealing with Antimony in Turkey

In Turkey there are increasing numbers of people, firms and state institutions working on the extraction and export of antimonial ores and manufacture of metal. Up to 1964 there were only two or three of such

(Recai Korkut - Bilecik Söğüt-Dudaş, Özdemir Antimuan Ltd. Tokat, Turhal) After 1965 this number increased up to eight. Between 1970 and 1974 there were sixteen firms and between 1974 and 1977 eleven. These numbers include firms which work with primitive methods. The operation and activity of these firms have been intermittent due to fluctuations of antimony ore prices. The leading firm in the mining and concentration of antimonial ores is Özdemir Antimuan Ltd., Mutlu Akü ve Malzemeleri A.Ş. is the major firm to produce metallic antimony. From 1975 on Etibank has started to produce metallic antimony in Halıköy Civa Işletmeleri. The important firms and their annual production capacities have been are as follows:

MUTLU A.Ş.	6800 tons/year
ALİ ALANYALI	1200 tons/year
MEFAŞ A.Ş.	200 tons/year
TERAKKİ MADENCİLİK	300 tons/year
ÖZDEMİR A.Ş.	400 tons/year
ETİBANK	5000 tons/year

(Antimuan, 1979). With these data at hand it is claimed that the total metal product capacity is very high, but not utilized. Occasionally Turkish metallic antimony is also sold to foreign countries. For example in 1977, 20 tons of metal is known to have been exported. Occasionally antimony metal is imported into Turkey, and metal ignots of foreign origin are sold by some merchants; in 1970-77 the prices of the imported metals have been two to eight times that of the foreign metal prices (Antimuan, 1979). Also in these years the prices of Turkish antimony metals in Turkey have been 20 percent higher than the prices of those exported (Antimuan, 1979).

Presently there are more than twelve firms which deal with the mining, concentration and export of antimonial ores and metal production:

1,2	Antimon Madencilik Ltd. Şti., Ivrindiği, Balikesir
4	Madsan Maden Sanayii ve Tic. Ltd. Şti., Ankara
4	Marmin Madencilik San. ve Tic. A.Ş., Istanbul
3	Mutlu Akü ve Malzemeleri San. A.Ş., Pendik, Istanbul
1,2,3,4	Özdemir Antimuan Maden Ltd. Şti., Istanbul
4	Petrometal, Ankara
1,2	Rasih ve Ihsan Maden Ltd., Istanbul
4	Saim Budin Madencilik San. ve Tic. A.Ş., Istanbul
4	Selsan, Madencilik San. ve Tic. A.Ş., Istanbul
3	Terakki Madencilik San. Ltd. Şti., Istanbul
4	Toroslar Madencilik ve Tic. Ltd., Adana
4	Ünimeks Kimyasal Ürünler Tic. ve San. A.S., Istanbul

1. Mining
2. Concentration
3. Metal Manufacture
4. Export

(Turkish Industrial Catalogue, 1983).

a) <u>Özdemir Antimuan Ltd.</u>

Of these firms Özdemir Antimuan Ltd. Şti. is probably the oldest. This firm started its mining activities in Turhal as early as 1933 and the first metallic antimony in Turkey was produced again by this firm in 1949 (Antimuan, 1979). The present installations are about 20-25 years old.

Before the new mill, the ores, above walnut size were handsorted to 10 to 20%Sb and the fines were dumped. The small lumps obtained so were smelted in a set of furnaces: two brick shaft furnaces and two soil-fired reverbatory furnaces. In the shaft furnace, lumps were mixed with coke and ignited. The antimony trioxide thus formed was recovered at various points at the foot of the upright pipes in a tubular system (probably a Herreaschmidt furnaces). The product mixed with soda, charcoal and iron fillings was reduced to regulus in the first reverbatory furnace followed by a second refining process in a second reverbatory furnace (refining steps known as singling and doubling). The process is reported to be wasteful (Finn, 1963).

The analysis of the metals vary slightly among samples but is claimed that the product contains not less than 99.5%Sb. Arsenic, iron, sodium and sluphur are primary impurities (As 0.29-0.41%). A very small amount of silver could be present.

The newer installation is an ore concentration plant consisting of a wet mechanical preconcentration plant, flotation cells and driers. The mechanical parts include an ore silo, screens, an impact crusher, symons cone crusher, concentration tables, jigs, a second silo and a wet tube mill and a rake classifier. The flotation system consists of fourteen cells each 1200 lt capacity (Finn, 1963). The reagents used in flotation are reported to be the following:

Sodium Silicate	1080 gr/ton
Flotanol F	810 gr/ton
Benzol	370 gr/ton
Creosote	430 gr/ton
Lead Nitrate	500 gr/ton
Copper Sulfate	1870 gr/percentage

The product analysis averages to 65%Sb, 0.4%As, 0.05%Pb and 0.01%Cu. An analysis of a batch is reported as follows:

Sb	64.79
S	26.23
Sn	0.16
Pb	0.04
Cu	0.01
As	0.57
SiO_2	2.44
FeO	2.02
CaO	0.16
Ag/Au	Nil

The mill is designed to produce a concentrate of 65%Sb, with feeds containing higher stibnite contents, the product quality rises to 66%Sb.

The Özdemir Antimuan Firm has rather specialized in the mining concentration of ores and sales of the concentrate in foreign and domestic markets. The old antimony smelting plant of this firm is reported to be out of operation. It is reported that studies have been made by this firm for the erection of a metallic antimony production plant (Antimuan, 1979).

The sales prices of the concentrates are usually based on the London Metal Bulletin. CIF prices (Europe) of concentrates above 60 percent antimony at the end of November 1984 fluctuated between $ 27.75/unit and $ 29/unit. At this time the respective price of rich ores were $ 28.75 to $ 31/unit. The price per ton of 65 percent concentrate based on $29/unit would thus be $1885. The price of 99.6 percent antimony metal at this time changed between $ 3275 and $ 3374 per ton (Barutçu, 1984).

b) Other Firms

Next to Özdemir Antimuan, Mutlu A.Ş. is the most important firm on the present antimony works in Turkey. It is reported that this firm obtains metallic antimony b yroasting stibnite concentrates to trioxide and later reducing the product. Due to the high capacity of these plants, the furnaces where trioxide is obtained should be of interest. Today due to the overcapacity of the antimony oxide plants of this firm, ores which belong to Etibank are processed on behalf of this state enterprise. It is reported by the sales officer of Mutlu A.Ş. that up to about one or two tons of antimony trioxide is sold to the market when demanded in Turkey. Today the sales price is 1650-1750 TL/kg. Metallic antimony is reportedly 2000 TL/kg when sold by this firm (wholesome F.O.B. prices).

Terakki Madencilik, Ali Alanyali and Etibank own the remaining smelting plants of interest in regards of production of antimony trioxide.

6. Specifications on Sales of Antimony Ores and Metals

The minimum concentration of concentrates in order to be marketable is 50 percent. Products with concentrations of 60-65 percent are known as good products. The products of this class are required to contain low Pb, As and Cu impurities. Some smelters accept these contaminations up to a level of one percent. The individual concentrations of these impurities are required not to exceed 0.2-0.3 percent (Antimuan, 1979). Some of the smelters tend to buy antimony trioxide instead of stibnite. The preferred antimony in such products are 81-83 percent. The reason for such a preference is due to restrictions on the SO_2 emittence of plants from roasting of stibnite. Antimony ores containing small amounts of impurities as oxides, chlorides and sulfides can be used in industry for the direct production of other antimonial chemicals. Such ores are required to contain no more than 0.25% of all foreign matters none of which exceed 0.1% in order to be marketable. Liquated stibnite (Crudum) is quoted or 70% Sb in the markets.

Many different kinds of metallic antimony can be found in the markets. The term "regulus" refers to metal antimony assaying 99.0% Sb containing no more than 0.3% As, 0.1% each of S, Zn, Fe and have a starry surface. Regulus grade antimony is marketable in metal stack exchange of London and Paris (Antimuan, 1979). The preferred metals in such markets contain a minimum of 99.5% Sb and a maximum of 0.2% As. Metals of 99.99% Sb can be found for special applications. The most famous metallic antimony is known as Cookson's C, other famous brands are LaLucette (French), U.S. Lane Star, U.S. RMM, Zacha (Jugoslavian) metals (Joseph, 1977).

B. METHODS OF OBTAINING ANTIMONY TRIOXIDE

1. Requirements on Antimony Trioxide

Antimony trioxide had first been manufactured as an intermediate in the production of metallic antimony. This oxide obtained from roasting of ores had minimum restrictions in quality. However the advent of the possible use of antimony trioxide as a white pigment in about 1844 (Price, 1943), pressed for improvements in product qualities of ore roasting plants. In 1880's a pure antimony oxide ore was imported into England (probably from China) and sold for making paint largely used for painting gasometers in London on account of its exceptional durability (Riker, 1933).

For many years attempts were made to produce antimony trioxide with suitable pigmentary properties for paints. Pigment grades of antimony trioxide originated in Europe (1920) and were successfully made in U.S. in about 1930 (Sward, 1944). The earliest such process producing pigment antimony trioxide with small differences was similar to the French Process of zinc oxide manufacture (Martens, 1968). In this process the vapours of metallic zinc were burned in air and the fumes collected (Calbeck, 1960). Successful and consistent manufacture of pigment grade antimony trioxide from ores through volatilization did evolve slowly was to be practiced much later.

Today antimony trioxide is still manufactured and marketed for production of metallic antimony. In the metal stock exchanges antimony trioxide is quoted as 81-83% Sb (97-99.4% purity). Lower grades though are still produced and are used applied successfully in reduction to metal. Metal bound trioxides do not have any requirements on uniformity of properties or crystal shapes, particle sizes and colour. The higher grades (in respects of purity) can always be used as chemical stocks. The grades to be used as pigments, fire retarding additives or catalysts need to be at least of 99% purity. The grades for these applications differ usually in the size and shape of the crystals (particle sizes) and the range and choice in tolerable limits of contaminants. For pigments cubic crystals (senarmonite) of average particle size of 1-1.5 micrometers are favored. Large particle sizes or needle like crystals (valentinite) are preferred for plastics where fire retardency but not opacity is needed. General fire retarding applications could also use fine particle sizes: less than 1 micrometer such as "Firemaster" (Glogger, et.al., 1975).

The basic contaminants of antimony trioxide are iron, lead, arsenic, sulfur trioxide (or sulfuric acid), copper and nickel. The most abundant contaminants are arsenic and lead. Arsenic, lead and acidity due to sulfuric acid are especially undesirable when the trioxide is to be used as a catalyst. The analysis of some of the commerical grades of antimony trioxide are listed in Appendix B.

2. Characteristics of Oxidation and Volatilization Processes

a) General Description and Difficulties

Oxide volatilization from ores or from metallic antimony is the principal method of antimony trioxide manufacture, and the process is the only pyrometallurgical method applicable to low grade ores. Combustion of the sulfide in the ore supplies some of the heat so that fuel requirements could be minor.

$$2Sb_2S_3(v) + 9O_2(g) \rightarrow 2Sb_2O_3(v) + 6SO_2 + 687 \text{ kcal at } 500°C$$

or $$4Sb(v) + 3O_2(g) \rightarrow 2Sb_2O_3(v) + 163 \text{ kcal}$$

Arsenic oxide can be removed because it is more volatile than antimony trioxide.

There are many variations of the volatilization process, the principals employed being the same but the equipment differing. If starting material is the ore, in all cases the sulfur is burned away (at roasting stage) and removed from the waste gases, while the trioxide (as in pure metal) which forms volatilizes and is recovered in flues, condensing pipes, a baghouse, Cotrell precipitators, or a combination of these. At high temperatures roasting and volatilization are usually effected almost simultaneously, especially by heating the ore in contact with coke, charcoal or sulfur with controlled aeration in equipment such as a shaft furnace, rotary kiln, converter or blast roaster. Usually the oxide produced in this manner is impure and used for reduction to metal, sometimes after briquetting. Better grades can be obtained by selection of charge and control of volatilization and condensation products (Carpella, 1981).

If the process is based on roasting of ores, depending upon grain size, oxidation can begin at 290 to 430°C and reaches maximum intensity about 500°C as proposed by Wang. Since, however, at these temperatures the vapour pressure of antimony trioxide is a low 0.0625 mm Hg (Hincke, 1930), satisfactory volatilization rate of antimony trioxide, and hence good recoveries are only achieved at 1000 to 1100°C (vapour pressure above 600 mm Hg, boiling point at 1570°C).

Since Sb_2S_3 (stibnite) has a boiling point of 857°C it is quite probable that at higher temperatures the above reaction takes place partly in the gas phase. There are, however, two complicating factors which require a fairly close control of this process.

1. Between 500 and 900°C if sufficient oxygen is present, Sb_2O_3 is oxidized to higher oxides (Sb_2O_4 and Sb_2O_5), which are nonvolatile and may be lost in the cinders. Above 930°C the higher oxides decompose with formation of Sb_2O_3 and liberation of O; this reaction is favored if no excess oxygen is present in the furnace atmosphere.
2. At 546°C Sb_2S_3 melts and tends to form oxysulfides with Sb_2O_3 (melting point of 66% Sb_2S_3, Sb_2O_3 mixture is 485°C). This reaction is more likely to occur with an air defficiency, and with high grade ores. It may produce a glass coating on the ore particles which can seriously impair the oxidation reaction and may furthermore lead to aceretions at the furnace walls and sticking of ore particles (Joseph, 1977).

Similar problems still pose at lower temperatures; when sufficient oxygen is present at around 350-400°C the sulfides and trioxides can easily form tetroxides. Also during doasting at low temperatures there is a great tendency for the ore to frit (sinter) and this necessitates constant rabbing of the in old furnaces charge. The presence of gangue renders the ore less liable to fuse, so that the process is most easily carried out with poor ores (Bannister, 1945).

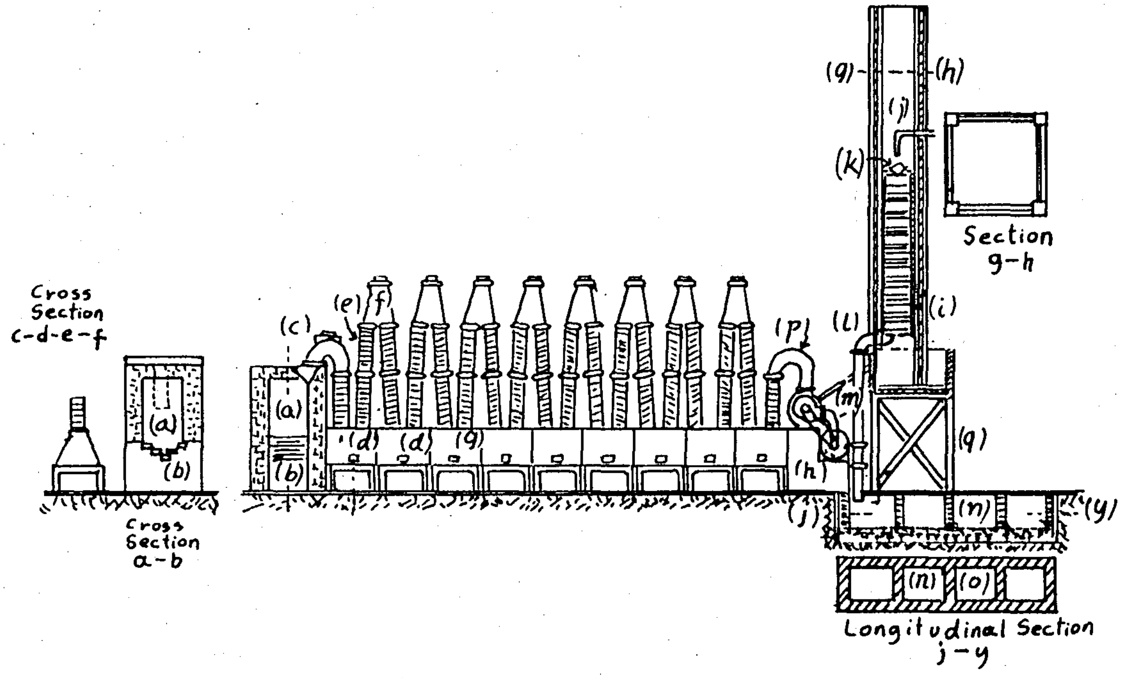
b) Description of Oxide Volatilization Processes

i) Antimony Trioxide from Stibnite Ores and Concentrates

The Herrenschmidt Furnace

In the early part of this century the roasting and volatilizing process was carried out in small blast furnaces followed by condensation pipes and a washing tower. The Herrenschmidt process was developed in the first decade of the century in La Genst, Mayenne, France. However it was chiefly been used in China as it had been simple in construction and easy in manipulation.

The roasting furnace was a rectangular shaft of fire bricks with a step grate of iron bars, provided with a hopper through which ore (pieces of 1 to 4 cm) mixed with coke or charcoal to maintain a suitable temperature and oxygen concentrations, temperature to be never over 400°C (Bray, 1941). When the stack furnace was properly designed so that the temperature in the central portion of the ore did not produce caking from fusion and if the depth of the combustion zone was so regulated that the antimony in the ore was completely volatilized its efficiency was high. Increased efficiency was also obtained if the furnace was relatively deep and not too large in diameter and if the area increased with depth so that in case of fusion the ore was not held by the side walls (Kohen, 1969). The gases were passed from the furnace into a chamber and then through a series of corrugated cast-iron tubes placed near vertical and air cooled (Figure 1). Below the lower end of the tubes the main portion of the trioxide was deposited. The last traces were removed by forcing the gases up a tower filled with coke over which water flowed. The draught was maintained by two centrifugal fans



(a) Roasting furnace
(b) Grate bars
(c) Goose neck
(d) Condensing chambers
(e) Condensers
(f) Cross-over
(g) Clean out doors
(h) Fans

(i) Coke tower
(j) Water pipe
(k) Distributor
(l) Discharging pipe
(m) Connecting pipe
(n) Settling tanks
(o) Partition
(p) Goose neck

Figure 1 Herrenschmidt furnace

(Bray, 1941)

working tandem. Under the lower end of the condensation pipes products varying in purity were extracted as a function of condensaing temperature and as a distance from the furnace. The first fraction contained a high ash content as well as higher oxides of antimony and PbO. The following fraction amounted to 40/50 percent of the total recovered was composed of practically pure Sb_2O_3 of minimum 82% Sb (98.2% Sb_2O_3) to be used or sold as such while the coldest fraction collected richest As_2O_3. Six tons of ore could be treated in 24 hours and the furnaces recovered over 90 percent of original antimony in the form of trioxide (Joseph, 1977; Bannister, 1945). Charge compositions obtained from different sources are as follows:

Ore containing 10-15% Sb mixed with 4-5% gas coke or 6-7% charcoal (Bannister, 1945)

Ore containing 15-25% Sb, 2-6% coke or charcoal (Joseph, 1977)

The limited output and the lack of flexibility led to the development of other processes.

The Chatillon Furnace

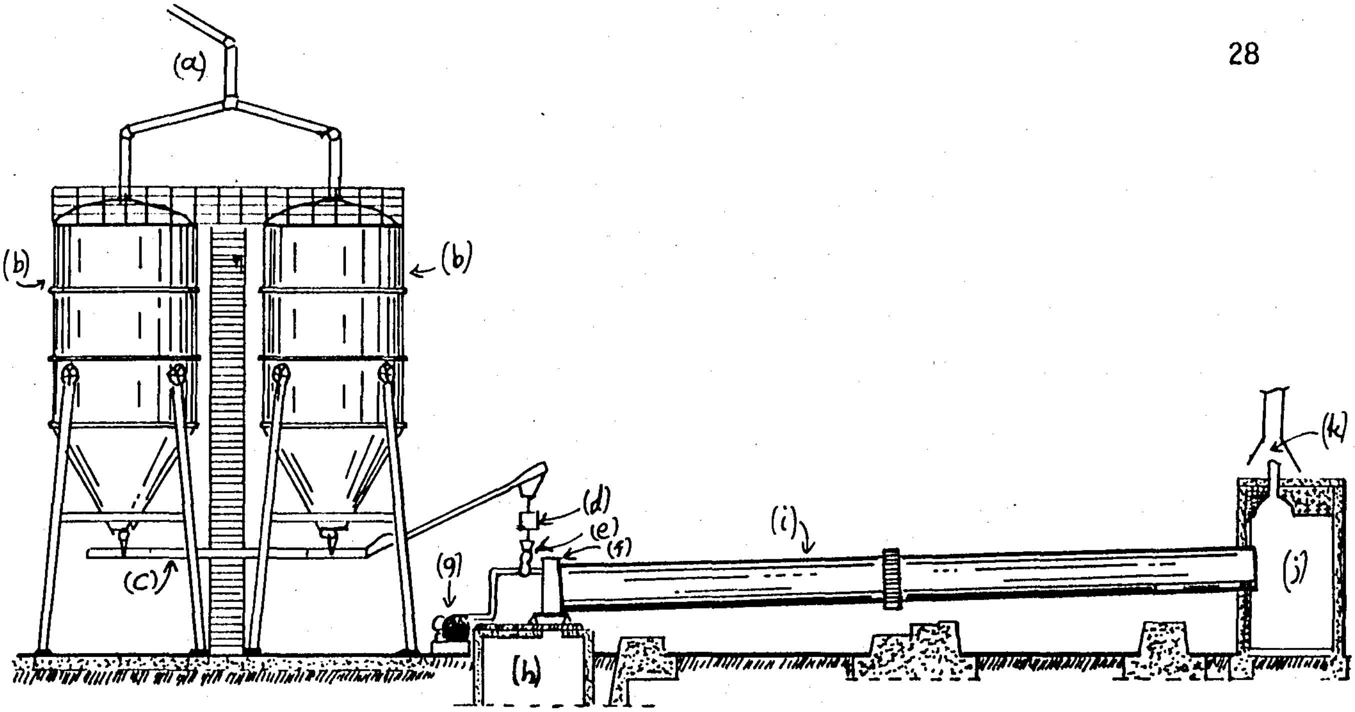
In the Chatillon process the volatilizing-roasting of the ore was conducted in a furnace made of two double cupolas, rectangular in cross section. A cupola is a small blast furnace, the function of which is to melt pig iron or scrap to make castings (Allexander, et.al., 1962). The dimentions of a cupola was reported as follows:

152 cm inside diameter, 4.6 m in height and 15 cm lining (Porter, 1912).

In the Chatillon furnace, the two upper furnaces opened into a flue which was common to both and terminated in a downtake through which fumes were led to condensing plant. Within the walls of the upper cupolas were vertical flues which communicate with the lower cupolas. Each of the lower cupolas was fitted on two sides with inclined bars forming grates, the other sides being of fire brick, thus forming a hopper. The bottom was closed by a plate of iron, an opening which the spent residue drops into a truck below. The furnace was charged with ore in lumps or as dust, and coke in alternate layers, and was penetrated by hot air from the lower cupolas; the sulfide was thus oxidized and volatilized as Sb_2O_3. The function of the lower cupolas was to receive the residues from the uppor cupolas, to complete the oxidation of any undecomposed sulfide and at the same time to cool the residue and heat the air supply to the upper cupolas (Bannister, 1945).

Rotary Kiln Furnaces

The previous furnaces were later replaced by rotary kilns. The idea of application of cylindrical rotary furnaces to roast stibnite belongs to Plews. The dimentions of the furnaces varied, 11.6 m to 26 m in length and 2 m in diameter. A 2 m by 26 m Waelz kiln could treat 10-15% Sb ore at a rate of two tons per hour. This type of furnace enabled continuous roasting of fines and concentrates without the need of briquetting. The early kilns were heated with a gas flame at the discharge end to a temperature of about 1200°C, 10-15% coal or coke was added to act as heating and diluting agent to avoid sintering of ore.



(a)	Duct for pneumatic haulage of fine material
(b)	Storage tanks - operating alternatively
(c)	Conveyor
(d)	Dosing scale
(e)	Injector-mixer
(f)	Burner
(g)	Compressor
(h)	Water fed discharge tank
(i)	Rotary kiln
(j)	Settling chamber for heavy parts
(k)	Inverted funnel to cool below 400 C

Figure 2 Rotary kiln furnace (U.S.Pat. 3 759 500, 1973)

In these furnaces Sb_2S_3 was first volatilized and later oxidized to Sb_2O_3 in an atmosphere containing CO, the trioxide was condensed and recovered in bag filters in high yields. However accretion which caused lenthy interruptions and maintenance frequently occurred until the development of modern rotary furnaces (Joseph, 1977; Bannister, 1945).

Direct fuel fired rotary kiln furnaces with slight modifications are still being used today. Such a furnace is now operated by Azienda Minerali Metallici Italiana (AMMS) in Italy for the manufacture of a high grade metallic antimony metal branded 'Stella'. This furnace is described in a Patent (U.S. Pat. 3 759 500) applied for in 1970. It is probably due to the operation of this kiln that the total metallic antimony production of Italy increased from average of 700 tons/year in sixties to an average of 1400 tons/year in seventies. This enterprise also sells antimony oxide under the brand name 'Stibal'.

This kiln (Figure 2) which has a length of 20 m, diameter, 1.2 m and a slant of 2%, consumes ores containing Sb 30-55% at a feed rate varying from 500 to 1000 kg/hr with an air feed at ratio equal to 2-3 cubic meters of air per kilogram of material feed. Under optimum conditions 54% Sb ore feed at 600 kg/hr is treated with 1200 cubic meters/hour of air. Fuel (naphta) consumption of 30 kg/hr and a vapour velocity of 2m/sec, with a yield of 98% to produce an oxide containing 76 to 81% Sb. The reaction zone of the kiln operates at 1200-1300°C by a burner and by the heat of oxidation of the material introduced. The fuel consumption is reported to be very low due to the exothermic reaction taking place so that the process is almost autogeneous. The oxidation of sulfide is characterized by an exothermicity of 1000-1300 kcal/kg of oxidized material (includes iron arsenic sulfur as well as antimony) (U.S. Pat. 3 759 500, 1973).

Modern Processes

Modern rotary furnaces operate with preheated air instead of direct flame and thus considerably reducing gas volume, and velocity (have less entrainment of ashes) and allowing a closer temperature/gas control without overheating of ore. The result is high throughput, high recovery, good flexibility with regard to ore grade (also high grade ores of 50% Sb and higher can be processed) allowing the treatment of mixed ores. The resulting Sb_2O_3 is relatively free from gangue constituents and from nonvolatile contaminations (Cu/Ni), the latter remaining in the residual calcine together with any precious metals.

The most novel method of antimony trioxide manufacture utilizes flash roasting of stibnite concentrates has been in operation since 1976 in Bolivia. There Bolivian flotation concentrates are treated to produce in the end 5000 tons/year of antimony metal and 1000 tons/year of antimony trioxide. Concentrates are injected (mixed with a flux and hot air) at high speed to a cyclone-shaped, water jacketed reactor in which instantaneous roasting and volatilization takes place with simultaneous melting of the gangue and nonvolatile metallic components. Molten slag and matter are precipitated from the gas stream and collected in an electric resistance heated forehearth from which both materials are tapped separately; the gases are reoxidized, cooled, and filtered in a gas dedusting unit yielding crude antimony oxide and the other volatile matter. The impure oxide is reduced to metal and refined for marketing and part of the crude metal is blown to Sb_2O_3 in a special oxidation furnace (Joseph, 1977).

Besides these methods other types of furnaces are also being used. Examples of such processes are: fluidized bed kilns and turbulent layer-kilns (U.S. Pat. 3 759 500, 1973). Fluidized bed kilns are especially interesting due to the possibility of better temperature control throughout the kiln.

Antimony ores or concentrates containing appreciable amount of As and Hg (which would unduly contaminate the resulting metal or trioxide) can receive a pretreatment by low-temperature oxidation at about 400 to 450°C, during which these impurities are largely volatilized without significant loss of antimony. This pretreatment could be carried in indirectly heated kilns under a controlled atmosphere in order to avoid excessive oxidation (like Sb_2O_3, it is the As_2O_3 which is volatile while As_2O_5 is not). Hg and As have to be recovered from the flue gases in a dust recovery system (Joseph, 1977).

Another method of manufacturing trioxide from stibnite involves oxidation in a rotary calciner between 650 to 1000°C to obtain impure Sb_2O_3 which in turn is further oxidized at 550°C to Sb_2O_4. Temperatures are then raised to 700 to 800°C to vaporize impurities; later tetroxide is reduced back to trioxide. The volatilized antimony trioxide is deposited in dust collectors as condensate (Hurley, 1977; U.S. Pat. 2 258 441, 1941).

Condensation Systems and Collectors

Condensation systems are those parts of the oxide volatilization processes where vapours are condensed. The systems differ in the speeds of cooling applied. Fast cooling results in very small particles which could be difficult to collect but be of preference when pigmentary products are required. Slow cooling results in large particles but enables easier fractionation and separation both from air and impurities. Fast cooling is possible with the introduction of a blast of cold air to the vapours. Slow cooling can be carried out in condensation pipes.

Condensation pipes are a set of long nearly vertical cast iron tubes connected in the ends thus resembling repeating letters of V or W. Each of the bottom of the vertices open onto a closed collecting chamber inside which a truck receives the products. The pipes are air cooled. This system has mostly been used for Herrenschmidt furnaces. Usually a second system of collectors are used for complete recovery. Condensation pipes always deliver the condensates to collecting chambers.

Collectors are those parts where gases are cleaned out of the particles they carry. Few of such apparatus are coke towers, bag filters, cyclone seperators and Cotrell precipitators.

Coke towers have mostly been used after the condensation pipes in the Herrenschmidt furnace to reduce the remaining 25% of volatile oxide to 10%. The coke towers used water flowing inside the surfaces to wash the vapours out of the combustion gases. They have proved to be inefficient.

Bag filters are very efficient but large installations and expensive maintenance is required. The bags are usually woolen. Instead of bag filters cyclone separators can be used with equal success. A special cyclone seperator has been designed called Warring Dust Collector whose main feature is that gas laden with particles are broken into a large number of small currents meeting each other so as to destroy almost entirely their original high velocity and thus causing deposition of dust.

The Cotrell process of precipitation of fume is most efficient and except for small and isolated smelters, should displace coke towers and bag filter systems. One precipitator (Societe Nouvelle des Mines de la Lucette à la Genest in France) was composed of two compartments, each contained 16 tubes of 30 cm internal diameter and 4.8 m in length, and in the middle of each tube a negative electrode of nichrome wire 2 mm in diameter. The gas treated contained on an average 10 grams of oxide per cubic meter which after passing through the apparatus was reduced to 5-10 miligrams per cubic meters (Bannister, 1945).

ii) Antimony Trioxide from Metallic Antimony

Advantages of This Method

This method of antimony trioxide production has been preferred for pigment quality products from 1920 up until at least to the end of the Second World War. C.W. Price has claimed that pigment quality antimony trioxide could only be produced by burning pure antimony metal under controlled oxidized conditions, and that product from the burning of antimony sulfide is not suitable for use as a pigment (Price, 1943). This point should definitely be true for metal bound antimony trioxides no matter how pure they are, however controlled cooling of antimony vapours could produce products with pigmentary qualities.

According to later reports antimony trioxide of pigment quality can be obtained by direct oxidation of stibnite though with difficulty since slight changes in the air flowrate could lead to products whose colour (whiteness) tends more to a pink cream shade. Production starting from metal could only be affected by impurities in antimony (Listrat, 1957).

Today a comparatively high grade oxide (when compared with metal bound oxides) is obtained by direct treatment of ores with special attention to choice of charge, volatilization conditions and selection of product. A high grade oxide of this type is 'Stibnox' of Cookson, employed widely in the U.S. for creamic and other uses except for most exacting pigments (Carapella, 1981; Carapella, 1986).

Methods of Metal Oxidation

According to Price, there is a sharp distinction between the production of antimony oxide and zinc oxide from metal; the comparatively refractory zinc oxide being produced by the controlled oxidation of the metal vapour whereas in the ease of antimony oxide, the oxide enters the condensing system as a true vapour in an oxidizing atmosphere (Price, 1943). This indicates that condensation is the critical part of the pigment manufacture.

The oxidation of metallic antimony can be done in two ways. One method is to vaporize purified molten antimony and oxidize the vapours in air (Colour Index, 1956; Martens, 1968). Another method is to burn the metal under oxidizing conditions (Gloger, et.al., 1973) by drawing air over molten antimony. The antimony trioxide laden air is then drawn through cooling pipes or bag-houses. There is always a possibility of entrainment of nonvolatile antimony tetroxide acceptable up to 1%. The most important stage in the production of pigment quality antimony trioxide is the rapid quenching of the vapors to obtain crystals of desired size.

There are interesting developments on the manufacture of pigment quality antimony trioxide. In Japan two patents have been applied for processes similar to above. In one Pb and 20-80% Sb were heated at 650-800°C to volatilize Sb with air or oxygen being blown over the surface of molten mixture to form antimony trioxide at a high yield, (Jpn. Pat. 79103 798) and in another, Pb and Sb were molten at 400-630°C and treated with air or oxygen to form senarmonite, valentinite crystals or their mixtures or mixtures of antimony trioxide and tetroxide to be used as fire retarding agent for plastics and pigments or catalysts mixtures of 60 (Sb); 40 (Pb) was treated at 550°C with air to produce up to 99.93% pure antimony trioxide (Jpn. Pat. 79153 798, 1978).

The above processes are interesting in comparison of others where manufacture of antimony trioxide from metal is reported to require temperatures higher than 1000°C (Kohen, 1969). High temperatures are required for volatilize of metallic antimony. See properties of antimony in Appendix A.

3. Other Possible Methods of Antimony Trioxide Manufacture

a) <u>In Laboratory</u>

There are other ways of producing antimony trioxide either starting from the metal or from the ore stibnite. Most of these methods are uneconomic in industrial scales. However they are of academic interest, practicable in laboratory and important in purification of antimony.

The first of these methods is the precipitation of antimony trioxide by addition of hot water onto a solution of antimony sulfate.

The reaction in effect is as follows:

$$Sb_2(SO_4)_3(aq) + 3H_2O \rightarrow Sb_2O_3 + 3H_2SO_4$$

The precipitate must be washed and treated to remove free acid, dried and disintegrated (Gloger, et.al., 1973). The antimony sulphate can be obtained from stibnite by the following reaction using concentrated sulfuric acid at 300°C.

$$Sb_2S_3 + 12H_2SO_4 \rightarrow Sb_2(SO_4)_3 + 12SO_2 + 12H_2O$$

If alkali or magnesium sulphate is present, the reaction is faciliated so that even with dilute acid at 130°C the reaction can proceed. It was claimed that ores could be used in this way as a means of extracting of antimony (Mellor, 1957). Pure antimony sulfate can be obtained from pure antimony trioxide by the action of hot concentrated sulfuric acid (Schenk, 1963).

The easiest method of preparing of antimony trioxide is by hydrolysis of antimony trihalide in water. When antimony trichloride is used as a starting material for hydrolysis first antimony oxychloride is formed which later further hydrolyzes to form valentinite antimony trioxide crystals. The product should be washed with ammonia to remove all halogen ions remaining (Schenk, 1963). Cubic senarmonite crystals for pigmentary purposes can be obtained using an alkali solution for the hydrolysis of antimony trichloride. This speeds the hydrolysis process so that formation of oxychlorides is minimum.

$$SbCl_3 + H_2O \rightarrow SbOCl + 2HCl$$

$$2SbOCl + H_2O \rightarrow Sb_2O_3 + 2HCl$$

$$2SbCl_3 + 6NH_4OH \rightarrow Sb_2O_3 + 6NH_4Cl + 3H_2O$$

Price gives examples of hydrolysis of antimony halides for the production of antimony trioxide of pigment qualities. When a dilute solution of sodium carbonate is used to aid hydrolysis of chlorides, better products are reported to be obtained. Antimony fluorides are shown to be better starting materials for the production of pigment quality trioxides. Antimony trifluoride does not hydrolyze when added to water no matter how dilute. The addition of alkali to such a solution precipitates very fine crystals of antimony trioxide. However Price also reports that volatilized products are still better in pigmentary qualities than hydrolysis products (Price, 1943).

The simplest method of obtaining antimony trichloride is to use metallic antimony and chlorine (Schenk, 1963).

One of the proposed schemes of refining antimony to a very high purity is by burning antimony metal to antimony oxide with selective recovery of the oxide, dissolving this oxide in pure hydrochloric acid, repeated distillation of the solution to eliminate impurities; hydrolysing the product to antimony trioxide and reducing the trioxide to metal using a reducing agent such as sugar (Jevtic, et.al., 1978).

b) <u>In Industry</u>

Solution of hydrochloric acids can easily be used in the extraction of antimony from ores, preferably concentrates. Stibnite can easily dissolve in hot and cold HCl solutions, liberating H_2S. However when Cl is added to the leach solution, elemental sulfur is formed instead of H_2S. After reduction to the trivalent state, the $SbCl_3$ can reportedly be purified by solvent extraction and subsequently recovered as oxychlorides or trioxide. HCl leaching can also be applied to oxide ores by recovery is lower and the higher oxides are practically insoluble (Joseph, 1977). Ores containing large amounts of high oxides can be treated with KOH solutions.

One interesting method proposed uses Cl_2 or HCl gas to leach sulfide ores to form high purity antimony trichloride and sulfur or hydrogen sulfide as separable by products. The high purity antimony trichloride may be hydrolyzed to form high purity antimony oxide (U.S. Pat. 3944653, 1976).

III. EXPERIMENTAL WORK

A. APPLICATION OF OXIDATION AND VOLATILIZATION

1. Stibnite as Raw Material

Due to the apparent success of a set up devised by Marko Kohen (Kohen, 1969) a similar one is employed in this work with slight modifications.

a) Summary of a Previous Experiment

According to the thesis work of Kohen an apparatus consisting of three conceptual parts had been made use of.

The air supplying part: This part was reportedly consisted of a blower compressor and a heater with which heated air blown at a rate of 28 lt/min was raised from abient temperature to 80°C. This temperature was claimed to be sufficient for the purpose. The heater is a copper tube wound up to two turns and placed on a sheet iron was heated by two bunsen burners.

The oxidation chamber: This part consisted mainly of a one liter Pyrex Brand Glass flask with three straight necks, heated by an electric mantle powered by a power regulator and including an iron-constantan thermocouple connected to a 0 to 500°C pyrometer. The central neck, airtight, allowed in a steel stirrer and another thermocouple enclosed in a glass tube.

The collecting part: This part consisted mainly of a pyrex condenser (air cooled) and a filter bag. The condenser had been connected to the oxidation chamber with a Pyrex Brand glass adaptor with suitable joints and connected to the filter bag via another glass adapter. The filter bag had been tightly woven white cotton fabric with 850 warps and wefts per square centimeter.

In this earlier work, different procedures had been tried to find one that would produce the best results. The roasting scheme decided to be the best was reported to be as follows:

After heating the ore past 223°C the evolution of SO_2 gas started which was allowed to leave the chamber through a rubber tube leading out of the laboratory. With this the contamination of the collecting apparatus was eliminated. Upon completion of the oxidation stage, the temperature was raised to above 323°C up to 450°C to volatilize Sb_2O_3 formed to collect it in the condensation tube and the filter bag.

After preliminary trials to determine the roasting scheme, the air flowrate was decreased (regulated) so that the product contained 99.26% Sb_2O_3 obtained with 5.96 liters/minute rather than 59% Sb_2O_3 and 41% Sb_2O_4 obtained with air flowrate of 28 lt/min. The reduction of air flowrate reportedly resulted in the collection of the product in the first adapter and condenser rather than in the filter bag. The yield was reported to be 92% starting from a concentrate containing 60% Sb.

b) Description of the Set-up

The apparatus employed for the present work consist of the following:

Portable Vacuum Blower (Cenco Cat. No. 93971): A small unit suitable both for vacuum (38 cm Hg) and pressure (up to 76 cm Hg). At full rate blows 0.028 m^3/min of air.

Spherical Mantle for Three Neck Flasks (Cenco Cat. No. 16495-5): A double mantle (380 W lower part and 140 W upper part) to hold and heat a 1 liter gas flask with three necks, equipped with an iron-constantan thermocouple.

Pyrometer (Cenco Cat.No.11-472-60): A temperature reader for heating mantles to read a range of 0-500°C from iron-constantan thermocouple, zero being the ambient temperature or reference. Two of such pyrometers are used for reading temperatures.

Power Input Controller (Cenco Cat. No. 80297): An instrument varying output voltage from 0-140 volts to supply power to the heating mantles. Two of such units are used, each for the lower and upper sections of the mantles. It is also known as "Powerstat".

Power Input Controller (Kardeş Elektrik San.): 'Variac', an instrument varying output voltage from 0-220 volts, supplying a maximum of 2700 watts. This instrument is used for regulating power to the air heating equipment.

Pyrex Brand Glassware:

Flask, 1 liter capacity, three straight necks, sides 24/40 center 35/45.

Condenser, west type, drip tip; inner and outer joints 24/24, 50 cm

Adapters, two way, angle type.

Filter Bag: An undyed plain cotton fabric cut and sewn in appropriate shape.

Air Heating Element: This is a small device made up of glass tubes and a nicrome electric heater resistance wire. A glass tube 30 cm in length was lined with a resistance wire of 24 ohms winded in helical shape. The two ends of the tube were joined with shorter pieces of glass tubing to serve as forepiece and endpiece for the air to go through. The endpiece was bent so as to lead hot air into the three neck flask through a rubber stopper which served as a seal. The two ends of the resistance wires were led out of the tube at the sealing joints to be connected with wiring to 220 V Power Input Controller (Figure 3). An experiment was performed to determine exit temperature for different power inputs (Graph 1). In Graph 1, the levelling off at high voltage ratings is due to power loss to surroundings through increased natural convection and radiation and decrease in residence time of air with increasing volume. The curve is for air flowrate of 25.2 lt/min measured at 11°C at the outlet of the system.

Stirrer: A steel stirrer blade has been used to agitate the ore in the flask. A seal made of Water-Glass-Feldspar cement has been used to cover the central neck allowing only the stirrer rod and thermocouple wires. The stirrer was Bird and Tatlock Cat. No. 333/0001 with variable speed controller.

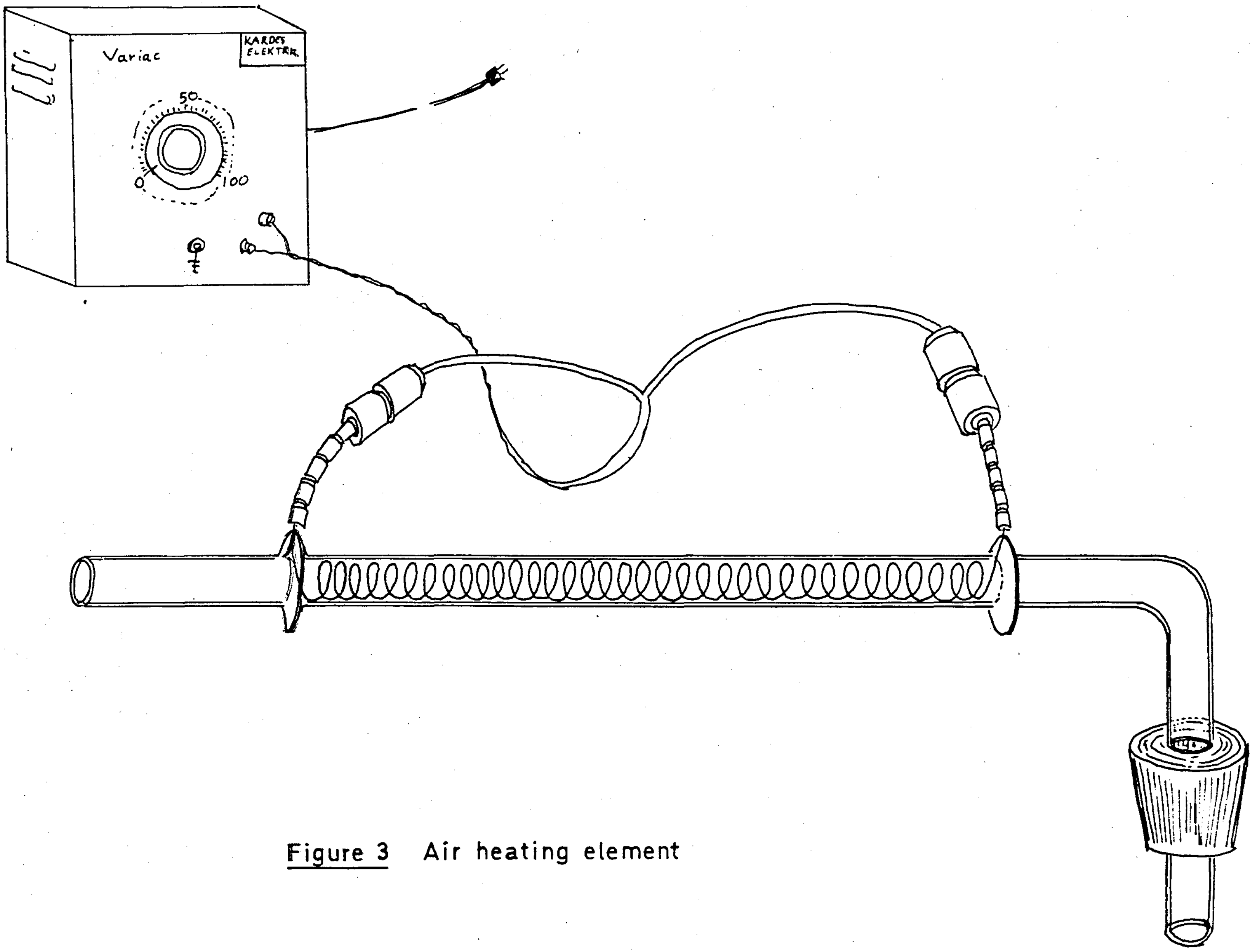
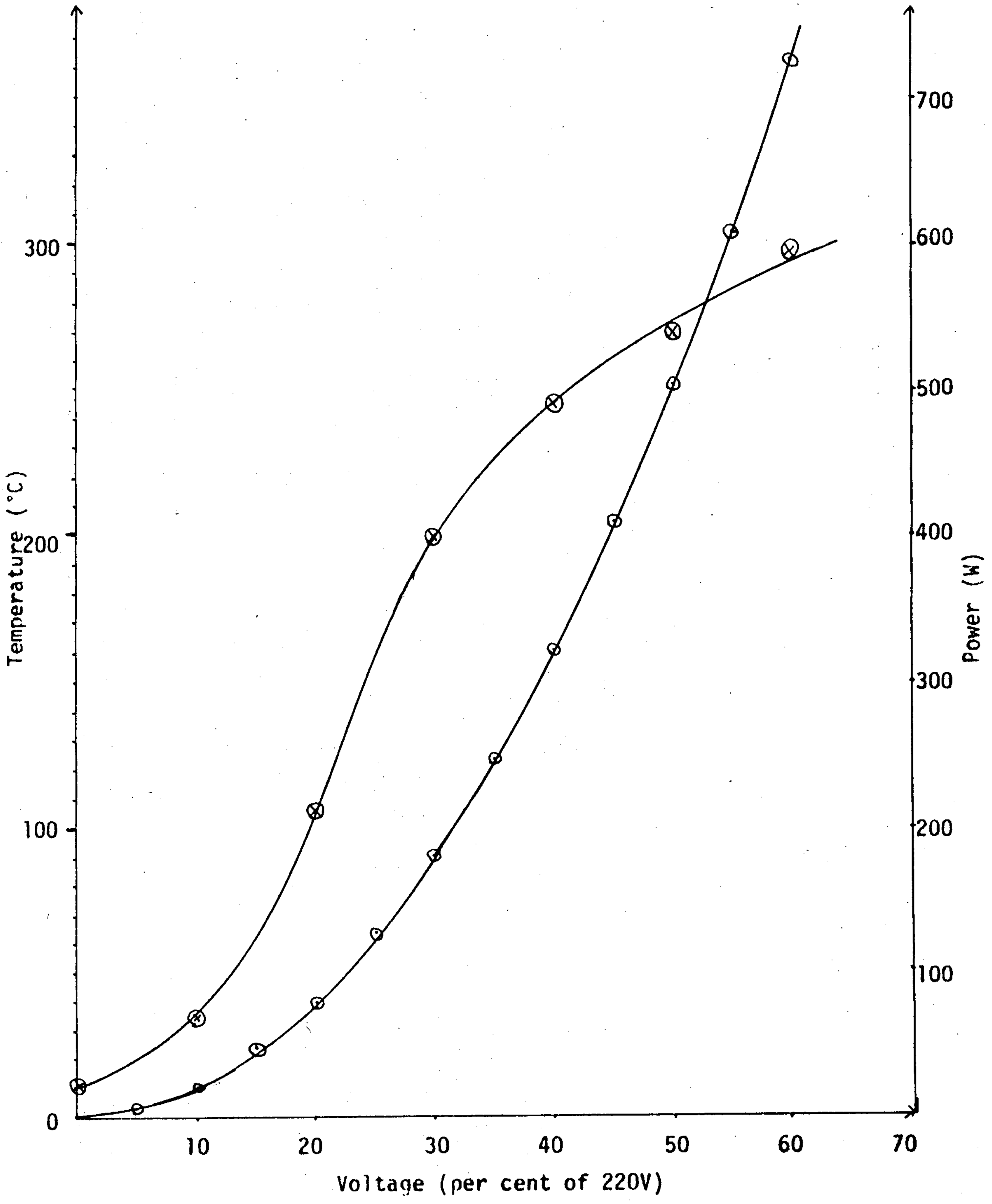


Figure 3   Air heating element



Graph 1 Power, temperature vs voltage curves for the air heating element

The arrangement of elements are shown in Figure 4.

c) Advantages Over the Previous Set-up

The main difference from Kohen's set is (Kohen, 1969) the use of an electric air heater with which it is possible to obtain any steady temperature up to 300°C. This enables better control of the air temperature and is a sufficient improvement over the sep-up on control of variables.

d) Raw Materials Used

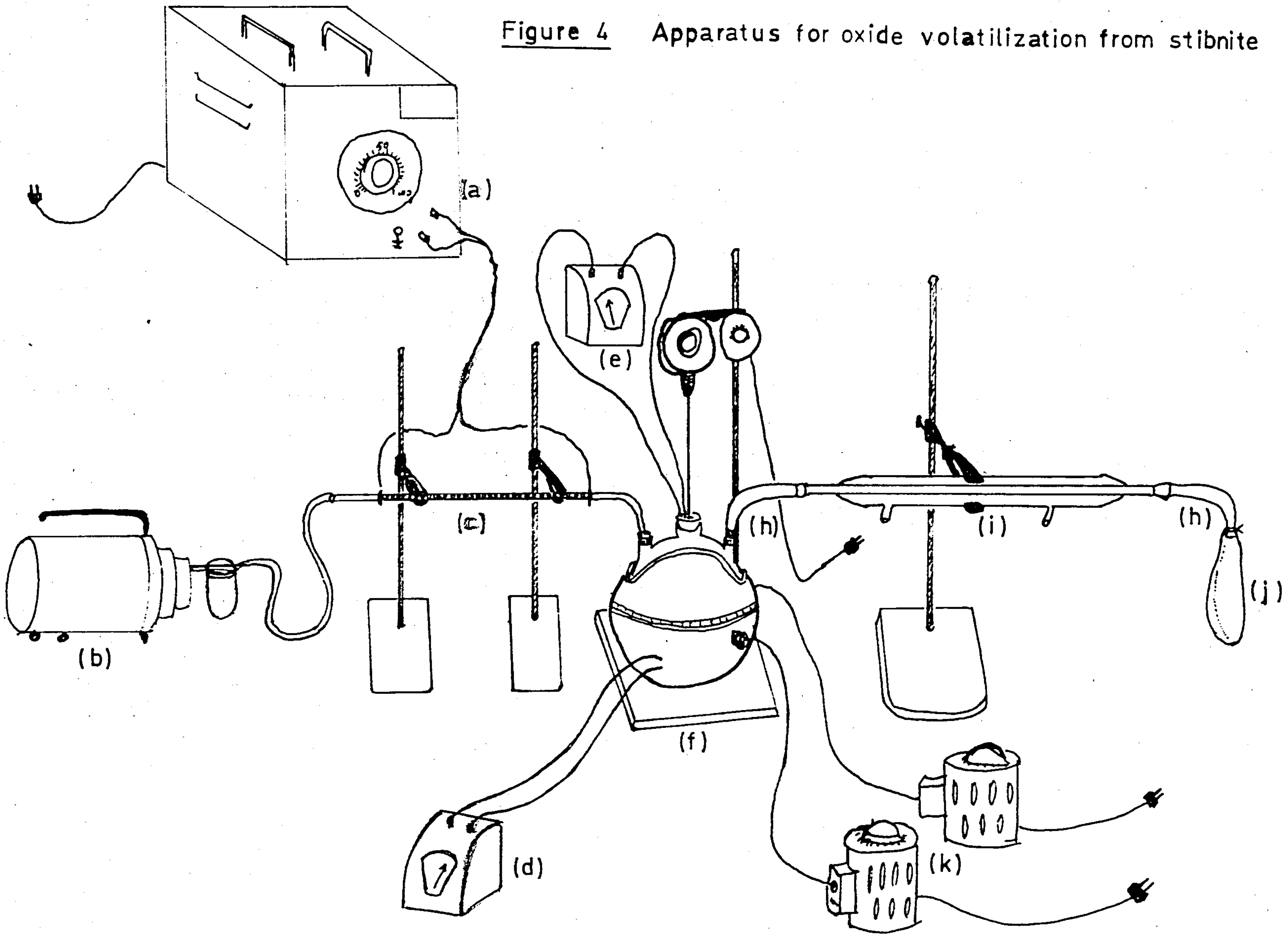
The most important part of the raw materials is the stibnite ores and concentrates which were obtained from Özdemir Antimuan Ltd. Şti. Four different samples of ores were obtained whose antimony contents were determined by the firm.

Sample	Sb in percent
1	5.66
2	11.30
3	16.15
4	19.77

The concentrate, about 400 gr analyzed to 66.73 percent Sb and 0.42 percent As. Also ground metallic antimony and a piece of metal ignot was available.

About 40 grams of a sample was used for each run of experiment.

Figure 4 Apparatus for oxide volatilization from stibnite



Description of Figure 4.

a) Variac

b) Air blower

c) Air heating element

d) Pyrometer for mantle temperature

e) Pyrometer for oxidation temperature

f) Spherical mantle enclosing a three neck flask

g) Stirrer and motor

h) Glass fittings

i) Condenser

j) Filter bag

k) Powerstats

e) The Experiment, Description of Difficulties and Results

All experiments were conducted with the aim of obtaining a product of pigmentary qualities. With this object, additives which could serve as fuel or oxygen consumers such as sulfur, gasoline or coal were not used in order to obtain products with best colors.

The resistance of the apparatus to a maximum of 500°C naturally restricted the operating conditions to low temperatures. However a range of 500°C was sufficient for the purpose of the experiment, namely being the investigation of production at minimum possible temperatures. The heating regime of the process which underlined the procedure was similar to that one determined and used by Marko Kohen.

First the material in the system was heated slowly up to 200°C with slow stirring (max. 60 rpm) after which hot air at 200°C was blown in. The exit gases were checked for the evolution of SO_2 by its particular smell. The presence of SO_2 in the exit gases indicated the start of oxidation.

As long as SO_2 was produced the exit gases were let out of the reactor without passing through the condensers or filter bags. The system was kept at temperatures between 200°-300°C as long as possible to get rid of SO_2 gases and As_2O_3 and other probable vapors.

When SO_2 was no more detectable the condenser system was connected to the reaction chamber. The temperature was risen above 300°C to volatilize and collect Sb_2O_3. Various problems arose with the method. The most serious of these was with the sintering of the charges. The stirring system was not efficient for the agitation of ore at too low speeds and at slightly higher speeds the ore started to fly out of the oxidation chamber. The stirring rod was seperated from the motor and was used as a hand instrument to pulverize the fused charge. When this also proved useless the charge was cooled, taken out of the chamber and ground to a reusable state. One such grinding step was sufficient to prevent resintering in a successive attempt of oxidation between 200-300°C. This step was repeated for all charges regardless of antimony content of ores, however the severity of the problem was least with 5 percent antimony ore.

Another difficulty was in the collection of oxide vapors produced. Most of the vapors produced were condensed and removed from the gas stream to cling on the walls of the condenser. A very small portion of the vapors reached the filter bag. Recovery of oxide from the walls after dissambling the apparatus resulted in partial loss of the product. This difficulty did away with any chance of yield analysis and quality determination. The color of the product as seen under the glass condenser always had a yellow shade and was never as white as a reagent grade samples.

The apparatus was slightly changed to aid the condensation of vapor and its collection in the filter bag. A second 1 liter three necked pyrex flask was installed in place of the condenser. The two side necks were used as inlet and outlet while the middle served as a part for a second stream of air to cool and condense vapors. The modification proved not useful.

To analyze the volatilization phenomenon individually, a batch of pure antimony trioxide (obtained from hydrolytic methods) was used instead of the ore. The chamber was heated beyond 300°C (Antimony trioxide is yellow at this temperature). Air was introduced at a rate of

28 lt/min at 300°C to carry the volatilized oxide to the condensing and collecting section. A very small portion of the original sample was volatilized to be condensed in the condenser. The rest of the material remained solid against temperatures as high and above 500°C. The remains were understood to be antimony tetroxide.

2. Metallic Antimony as Raw Material

An apparatus is built to observe the production of antimony trioxide from metallic antimony. The assemble consisted of the previously described air blower, air heater, a bunsen burner (Mecker type). Two pyrex brand joints (fittings) and a water cooled condenser and a filter bag. The set-up was held by clamps on stands in the manner shown in Figure 5.

A piece of antimony metal (5-10 grams) was placed on the elbow of the Pyrex Brand fitting. The bunsen burner just under the elbow heated the metal to a temperature above its melting point. After the metal was molten, hot air (~150°C) was blown into the system. White fumes formed and condensed on the walls of the system. A very small portion of the fumes reached the filter bag. After ten minutes of operation, a few grains of oxides were collected from different portions of the condenser. The color and physical shape of the product varied with these different portions. Even the whitest fractions had a yellow tint. Almost all of the product obtained consisted of minute coagulated crystals which indicated large particle sizes. In one portion of the condenser a mass of needle shaped long crystals (about 2-3 mm) were collected. The apparatus was not useful for any small scale production.

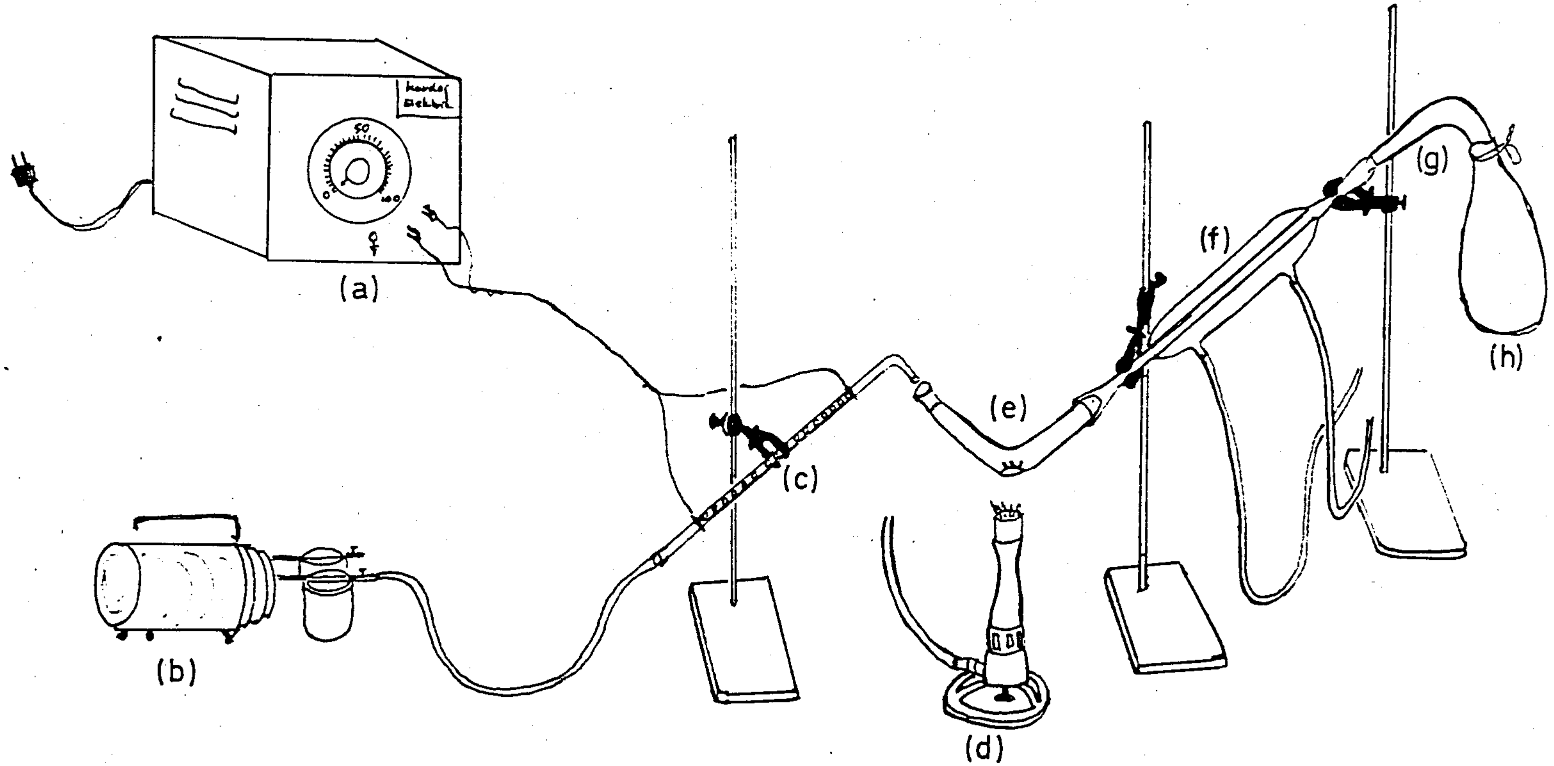


Figure 5 Apparatus for oxide volatilization from antimony.

Description of Figure 5.

a) Power regulator

b) Air blower

c) Air heater

d) Bunsen burner

e) Pyrex brand glass fitting

f) Pyrex brand water cooled condenser

g) Pyrex brand glass fitting

h) Filter bag

B. APPLICATION OF HYDROLYTIC METHODS

1. Description of the Method

Antimony trioxide is also attempted to be made from hydrolysis of antimony trichloride. The main reason behind this involvement was the desire to obtain pure antimony trioxide to be used as standard for analysis of antimony trioxide produced by volatilization process. Antimony pentachloride and tetroxide were also planned to be made along the trioxide with wet methods to determine spectral curve of each compound and compare with those of volatilization products.

Antimony trichloride has been prepared according to a procedure described by Schenk (Schenk, 1963) by reacting chlorine gas with ground metallic antimony. Part of the product is purified and hydrolised as described again by Schenk (Schenk, 1963).

2. Preparation and Purification of $SbCl_3$

a) <u>Description of Apparatus and Raw Materials</u>

The following instruments have been used for the set-ups:

A 1 liter distillation flask with a side arm at 75° angle,
A Hempel distilling tube,
Filtration flasks, 500 ml capacity,
A pear type fractional distilling column,
A flask with a three way stopper enabling connection either from a funnel reservoir or from an outlet to which a PVC tube can be installed. The flask is used as a gas generator.

Condenser, West type dip trip, and appropriate adapters,
Thermometer, 0-250°C range,
Electric heating mantle equipped with pyrometer and power regulator,
A pyrex brand single neck, 1 liter round flask,
Boiling chips, Bunser Burner,
Rubber stoppers, PVC tubes, glass tubes and a bulb,
Appropriate stands and clamps.

The raw materials used were pulverized metallic antimony, concentrated hydrochloric acid and sulphuric acids, potassium permanganate crystals.

Three seperate set-ups have been used successively. In the first one (Figure 6) antimony trichloride was synthesized and in the second and third the product was purified by distillation (Figure 7 and Figure 8).

The first set-up can be analyzed in two parts. In one part chlorine gas is generated and purified and in another antimony powder and chlorine are reacted. Two gas wash bottles were made from the filtration flasks. In each bottle the mouth is sealed with a rubber stopper (wrapped in teflon tape) allowing a glass tube inside. $SbCl_3$ synthesis part consists of the distillation tube with side arm and Hempel distilling tube. The flask is clamped on a stand with a slant between 30 and 40 degrees. The Hempel tube is fitted inside so that the constricted end reaches the middle of the spherical part of the flask. The space between the flask and the Hempel tube is closed gastight with a rubber stopper wraped in a teflon tape. The open end of the tube is closed losely with an appropriate rubber stopper wraped also in teflon tape. The

a) Flask with three way stopcock
b) First wash bottle containing water
c) Second wash bottle containing sulfuric acid
d) Distillation flask
e) Hempel distillation tube
f) Rubber stopper
g) Rubber bulb

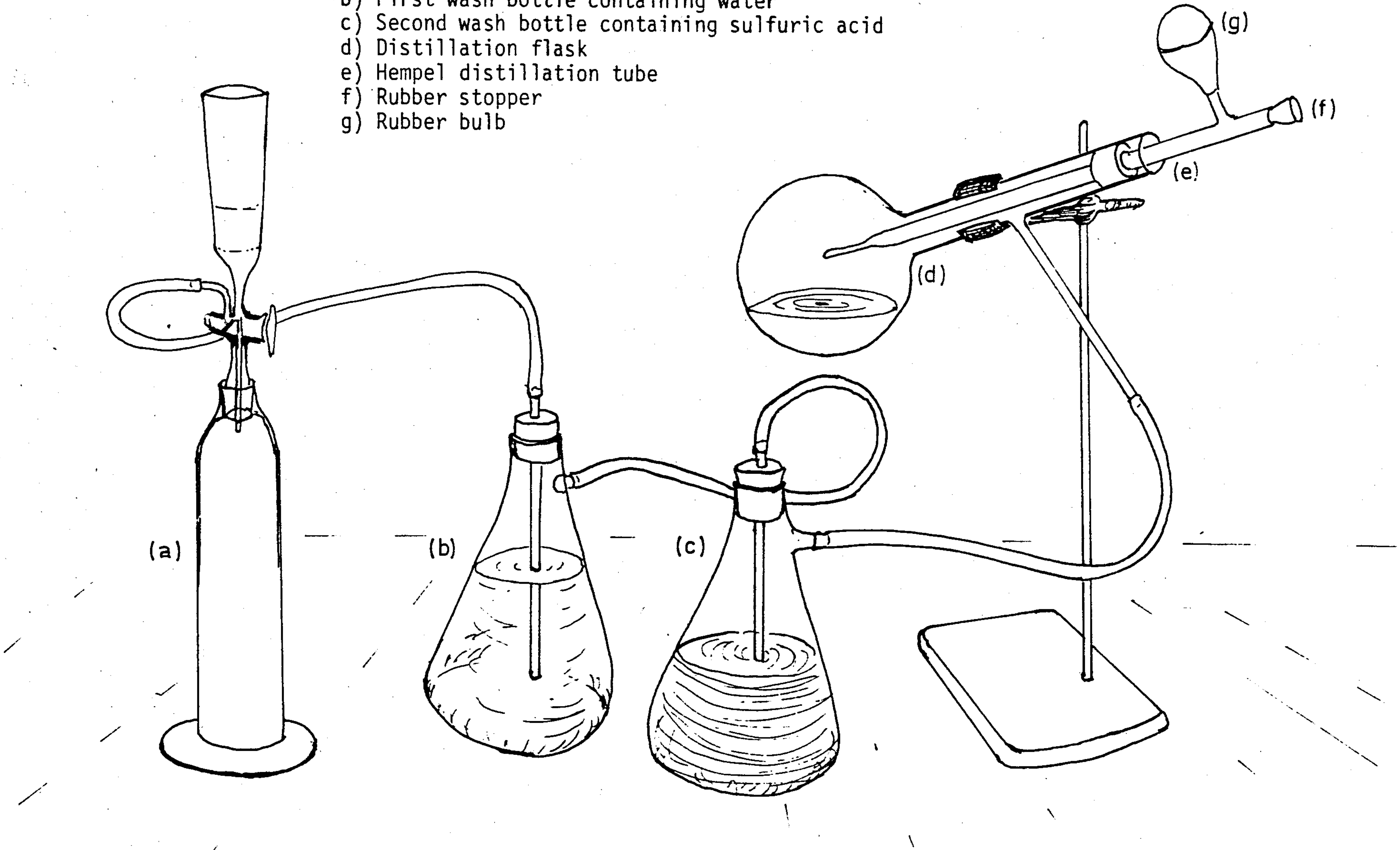
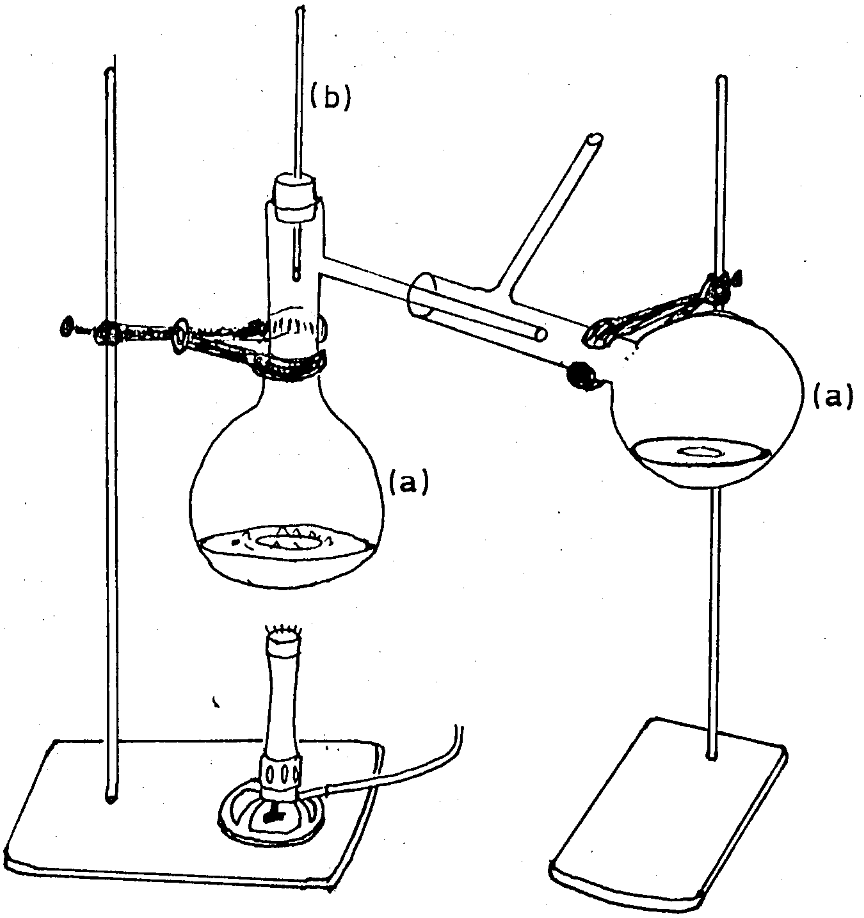


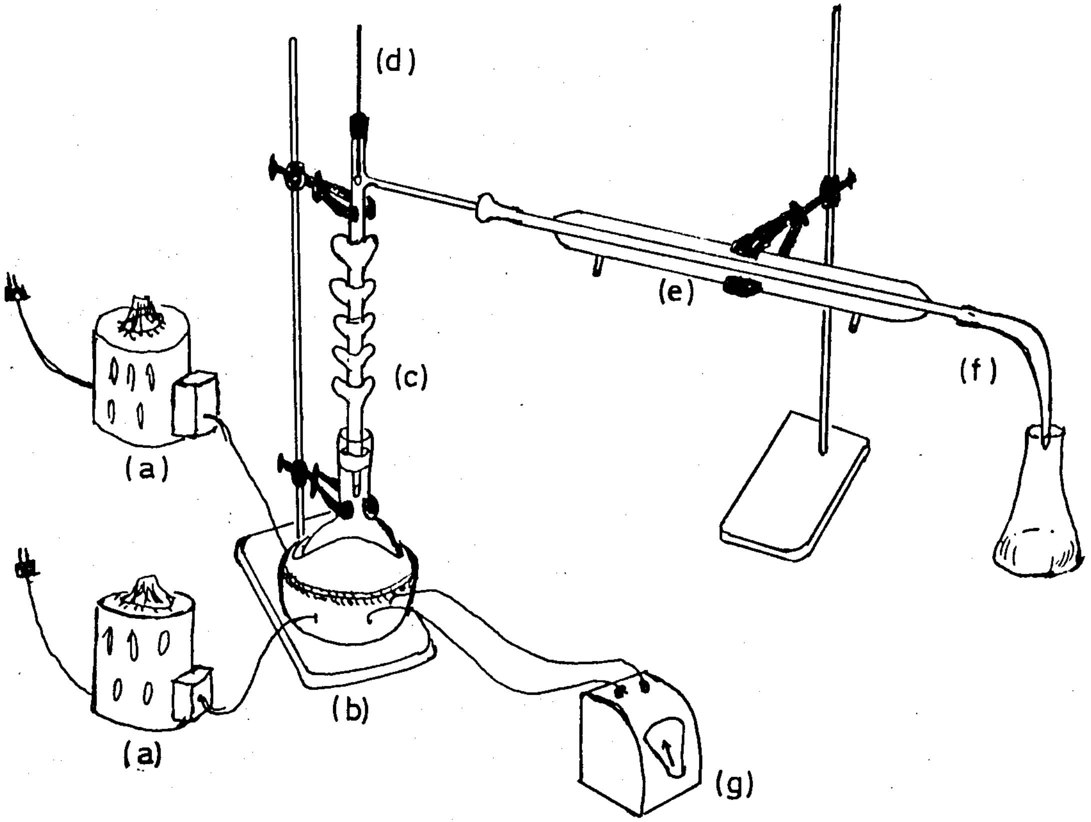
Figure 6 Apparatus for antimony trichloride synthesis.



(a) Distillation flasks

(b) Thermometer

Figure 7 Apparatus for antimony tricloride distillation (Part 1)



(a) Powerstats
(b) Spherical heating mantle enclosing a single neck round flask
(c) Pear type distillation column
(d) Thermometer
(e) Condenser
(f) Glass fitting
(g) Pyrometer

Figure 8 Apparatus for antimony trichloride distillation (Part 2)

The side arm of the Hempel tube is shortened and closed losely with a rubber bulb. The side arm of the distilling flask is connected to the suction port of the filtration flask with a PVC tube and similarly the glass tube installed in this flask is connected to the suction port of the remaining filtration flask. The glass tube emerging from this flask is connected to the port of the gas generating equipment.

The second set-up is shown in Figure 7. A bunsen burner is used to heat and distil the product for purification from impurities present in the original metal. The product is later distilled in apparatus shown in Figure 8. This time a pear type distilling column is used on a single neck flask heated with electric mantles.

b) Procedure and Results

The chamber of the gas generator is filled with $KMnO_4$ up to one fifth of height. The funnel is filled with concentrated HCl, the first wash bottle is filled with water and the second with concentrated H_2SO_4. Ground metallic antimony is placed in the Hempel tube from the port where loose rubber stopper is placed. This stopper is not inserted back until air is driven off the system. The three way stopper turned to let HCl solution drip onto $KMnO_4$. Cl_2 gas immediately forms. The gas is given way into the PVC tube which leads to the first wash bottle where any HCl gas present along with Cl_2 is dissolved. In the second wash bottle H_2SO_4 dries Cl_2 gas from any traces of water present. Dried Cl_2 gas reaches the side arm of the slanted distillation flask filling the spherical flask and driving air out through the open Hempel tube. The port of the Hempel tube is closed and air in this column is removed with the bulb by discharging into the ventillation system of the hood where the apparatus is assembled. Chlorine gas displaces air in the column and reacts with the graund antimony. The reaction can be described as burning.

$$Sb(s) + Cl_2(g) \rightarrow SbCl_5(l) + 104.8 \text{ cal} \qquad \text{(Mellor, 1957)}$$

The product is a green liquid which tricles down the column and drops into the spherical distillation flask. More HCl solution is poured over the $KMnO_4$ to produce Cl_2 gas in the gas generating flask. This flask is swirled from time to time to enable completeness. When the rate of Cl_2 gas evolution decreases more $KMnO_4$ is filled into the flask or the flask is decanted before reuse. The pressure in the system can be adjusted by sucking or blowing with the bulb on the Hempel tube.

The process is continued until the product collected has a depth of 4 cm occupying a volume of 250 ml at the end of a sum of 48 hours of continuous attention. The product obtained was nontransparent dark-green solution. The distillation flask is dismantled the Hempel tube is removed and powdered antimony is added on the liquid product until no more of the added antimony reacts with the solution. This product obtained solidifies upon cooling below 70°C.

The distillation flask is closed with a rubber stopper (with a thermometer) and is distilled two times with simple distillation. Powdered Sb metal is added to the system to minimize decomposition. The product is redistilled twice with a pear type distillation column. The fractions obtained below 210°C are all discarded. The condensation temperature of the product never exceeded 214.5°C. The product obtained collected in several erlenmeyers and is tightly closed and kept in a desiccator. $SbCl_3$ when pure forms colorless transparent crystals when solid. The product obtained at the end of final distillation was slightly colored most probably due to the presence of dissolved rubber from the rubber stoppers used. Purification by sublimation was attempted unsuccessfully.

3. Hydrolysis of $SbCl_3$ to Sb_2O_3

Hydrolysis of $SbCl_3$ to Sb_2O_3 is the easiest way of obtaining antimony trioxide. The procedure followed was about the same as that one described by Schenk (Schenk, 1963). The crystals of $SbCl_3$ (175 gr) is dissolved in concentrated HCl. The solution is diluted with distilled water until oxychlorides just start to precipitate. The solution is poured into a large volume of water (2 lt) in agitation. In a few hours the oxychlorides settle at the bottom of the container. Liquid above the precipitate is decanted and replaced with distilled water. After successive decantation the product is dried in 110°C oven.

The product obtained was slightly yellow in color when taken out of the drying oven. Under light the surface of the product darkened to a very light gray-brown color. Below the surface of the mass the earlier color persisted. This indicates that the product was not stable against light. Such a hydrolysis is known to result in metastable valentinite (rhombic) crystals of Sb_2O_3 (Schenk, 1963). The product qualities did not change when heated with a solution of NH_4OH.

A similar batch of $SbCl_3$ hydrolyzed in diluted NH_4OH gave products with better qualities. Products of hydrolysis took longer time to precipitate indicating presence of smaller crystals. This product did not show any reaction against light and was much brighter in whiteness than the valentinite crystals.

C. DESCRIPTION OF ANALYTICAL METHODS

Various analytical methods are available in determining the composition of antimony and antimonial products. Some like atomic absorption spectrophotometry utilize expensive equipment. Volumetric methods are also available and only some of these require expensive reagents.

1. Analysis of Ores and Concentrates

Ores of antimony are usually analyzed for Sb and As content. Complete analysis can be lengthy enough to include Pb, Cu, Fe, Ag, Au, Bi, S and Silica.

2. Analysis of Metallic Antimony

Analysis is conducted to determine besides Sb can led, As, S, Cu, Fe, Ni, Ag and Sn.

3. Antimony Compounds

Antimony compounds are analyzed for Sb and for its different oxidation states, As, Cl, SO_4 ion.

a) Antimony Trioxide

Sb_2O_3 may be analyzed for Sb by an iodine titration method. Sb_2O_5 may be assayed by a thiosulfate method. An abbreviated procedure for determination of Sb in Sb_2O_3 is as follows:

Accurately weigh between 0.25 and 0.30 gr of sample, dissolve in 5 ml HCl and add a solution of 5 g of KNa.Tartarate dissolved in 30 ml of water. Neutralize with cold saturated solution of $NaHCO_3$ and add 15-20 ml in excess. Titrate immediately with 0.1N iodine using starch indicator solution.

$$\% \ Sb_2O_3 = (\text{ml of } I_2)\frac{(0.07288) \times 100}{\text{wt of sample in g}}$$

Sulfate in Sb_2O_3: Add 10 g of sample to 100 ml of water containing 2-3 g of sodium carbonate, heat to boiling, boil for 10 min, cool and filter. Dilute the filtrate washings to about 125 ml, acidify with HCl and add 1 ml in excess. Heat to boiling, add 10 ml of 10% $BaCl_2$ solution, allow to stand overnight at room temperature. Filter the solution through a close textured filter paper, wash thoroughly and place the filter paper into a tared weighing crucible, ignite, cool and weigh.

$$\% \ \text{Sulfate} = (\text{wt precipitate}) \ \frac{(0.4115) \times 100}{\text{sample of wt in grams}}$$

A good collection of analytical procedures are given in Encyclopedia of Industrial Chemical Analysis (George, 1968).

IV. USES OF ANTIMONIAL COMPOUNDS

A. ANTIMONIAL PIGMENTS

1. Pigments

Pigments are powdered materials intended to be dispersed in liquid or solid binders for the production of surface coating products, plastics and rubber materials, textiles. Each of the field of applications could use the same compounds as pigments while requiring different forms of it. However pigments are generally manufactured for surface coating products and paints in particular. The conditions for a pigment to be in this field of application needs further description.

2. Pigments for Surface Coating Products

Surface coating products, paints, incs and enamels are balanced mixtures of resins, drying oils, pigments, driers and other constituents aiding the formation of the mixture. Of these, pigments can be organic or inorganic. Inorganic pigments can be prime white pigments, pigment extenders or colored pigments. In any particular paint the first two of these, prime white pigments and extenders are almost always present.

Prime white pigments besides imparting white color to the paints act as a hiding agent or opacifier. Pigment extenders are cheap fillers introduced to the system to modify the bulk properties of the vehicle, enabling easy applicability, better flow properties and to control textures of the resulting films.

Titanium dioxide, zinc oxide, zinc sulfide, basic lead carbonate and antimony trioxide are the most famous primary white pigments sometimes used individually or as mixtures. Barium, calcium, magnesium carbonates and sulfates, silica are typical pigment extenders. The choice of pigments or their mixtures are made so that of the resulting product, color is at its maximum whiteness, hiding power is highest, while at the same time possessing suitable surface characteristics, color retention and life span and economicality.

a) Spectral Characteristics

The spectral characteristics determine the color of a pigment. The term color applies to only the visible portion of the electromagnetic radiation. However in some applications spectral characteristics of pigments beyond the visible range of wavelengths are of interest. Color is usually a combination of different weights (percent reflectence or transmittence) of different wavelengths. A blue pigment usually has a dominant reflectence at shorter wavelengths. A red pigment on the other hand has dominant reflectence on longer wavelengths. A pigment which reflects all wavelengths at the same reflectence has a gray color. If such a "gray" pigment has highest possible reflectivity its color is white. Materials with white color are zinc oxide, lithopone, titanium dioxide, antimony oxide, precipitated calcium and magnesium carbonate and magnesium oxide. All of these materials are white in powder form. The brightest among these is magnesium oxide and is used as a reference white reflectence standard. The preparation of this standard is described in ASTM E259-66. The spectrophotometric method for the determination of reflectences is described in ASTM E 308-66.

b) Hiding Power

The ability to obscure or cover up is preferably called hiding power. The hiding power of a pigment is usually expressed as the area hidden by a unit weight of pigment when applied in the form of a paint or lacquer. Hiding power is usually expressed in terms of area per unit volume of point combined with the method used in measurement. Typical methods are ASTM D 406-39, Gardner Method, Haslum Method, Hallet Method (Mathiello, 1950).

All materials used as white pigments are more or less transparent. A portion of light falling upon a pigment particle is absorbed as heat, a portion is reflected and transmitted. By complete hiding it is meant that no perceptible light which has passed through the pigment to surface is to return to the eye. From this it can be understood that the pigment giving maximum back reflection and scattering per pigment volume and minimum transmission will give maximum hiding. Two different properties of a pigment determine its hiding power. These are particle size and indices of refraction.

Considering particle sizes, hiding power increases as particle sizes reduces to the order of wavelengths. Light travels through the paint media striking surfaces of pigment particles and only partly reflecting. As the number of particles increase the surface on which light refracts increase; thus, reducing the intensity of the conducted light. According to early experimentalists (Mattiello, 1950) the optimum size of white pigment particles is 240 nanometers for maximum opacity. Authors do not agree on this particular diameter but a range of diameters which lies between 200 to 300 nanometers is best. The optimum size for a particular wavelength according to modern theories depends on the index of refraction of the particular pigment. An approximation of particle size may be obtained by the use of average diameter. The complete story can be told only by a distribution curve showing the amount of material at each of the several sizes, often represented as cumulative curves or as percentage by weight per micron.

There are various methods of determination of particle sizes of fine pigments. The use of sieves is limited to the measurement of coarse particles which are objectionable in the final film. Microscopic measurement has problems. The resolving power of a microscope (at 1500 magnification) is theoretically 250 nanometers with visible light and the practicle limit 400-500 nanometers. Electron microscopes can work down one nanometer but the instrument is expensive and requires skilled operators. Visual counting is also tedious. A relatively cheap method is the sedimentation analysis. It has the great advantage of giving a direct picture of the particle size distribution without the tedious counting and measuring of a large number of particles as in microscopal method. The weakness of this method is that the formula used assumes spherical particles and for particles less than 1 micrometer determination may take about 48 hours. The Andersen pipette method is the simplest of the sedimentation methods. There are also so called adsorption methods which compute surface area per mass. Knowing density, diameter of the particles can be calculated. The most modern technique is electrical counting and sizing applied in what is known as a Coulter counter.

The second property that determines opacity is the difference in the index of refraction of the pigment and the vehicle. Index of refraction is the ratio of velocities of light in two different media as for example water to vucco. The ratios of indices of refraction determine the angles of refraction depending on angle of incidence of light at a boundary. When the indices of refraction of two media are close or the same, light passes through them without any change in its direction so that the interface between the madia becomes invisible. In this condition if a transparent and clear object is immersed in a media whose index of refraction is close to that of the object, the object will appear invisible to an observing eye. This ilso holds true for opacifying pigments. Indices of refraction of vehicles and pigments need to be different from each other for angles of refractences and thus scattering being maximum in the paint media.

The standard method of determining refractive indices of small solid particles is by immersion. In this method a few particles on a slide are covered with a drop of liquid, and observed under a microscope. In general, it is possible to tell whether the solid or liquid is of higher refractive index, and the later is accordingly changed until certain optical tests show that the particle and the liquid have the same refractive index. The index of the liquid is then easily determined to a high degree of accuracy (Cooper, 1948).

It is often stated that the hiding power is dependent on the refractive index differences ($n_p - n_b$) but this is an oversimplification. Earlier and more recent investigation has shown that scattering is a function of the well-known Lorentz-Lorentz expression

$$M = \frac{(n_p/n_b)^2 - 1}{(n_p/n_b)^2 + 2} \qquad (4.1)$$

The greater the value of M the greater will be the scattering and hence hiding power. Hiding power on the other hand increases with decreasing size down to a certain limit since the number of reflective surfaces increases with diminishing particle size. Reflectivity of surfaces has a positive contribution in the conduction of light in a mass of pigments. On the basis of experimental work an empirical formula is derived that determines optimum particle size for a pigment that gives minimum scattering

$$D_{optim} = \frac{\lambda_i}{1.414\ \pi\ n_b\ M} \qquad \text{(Nylen, 1965)} \qquad (4.2)$$

c) Other Properties of Pigments for Surface Coatings

A dry pigment in the form of a powder generally consists of agglomerates within which spaces are filled with air (The strength of forces holding the agglomerate together could vary with pigments).

Pigments which are prepared by precipitation are agglomerates in dry state. The optical properties of paints whose pigments are in this state is poor. Generally the vehicle and pigment are combined and milled in order to produce finely dispersed particles of pigments in paint. This grinding is done in different kind of mills for different durations for different kinds of pigments. The object of grinding is usually breaking the agglomerates into primary particles, increase wetting by displacing water or air and stabilization of dispersions. Sometimes wetting agents are also added to paint.

Oil absorption is another aspect to be considered. It is defined as the minimum amount of oil which is required to convert a given weight of dry pigment to a stiff but coherent paste. The oil absorption is normally expressed as grams of mililiters of linseed oil of definite acid value per 100 grams of pigment. This value is often used in comparing different batches and deliveries of a given pigment or to characterize pigments. It gives a rough idea on dispersability of a pigment, it also indicates the relative quantities of binder and pigment to be used for paint formulation.

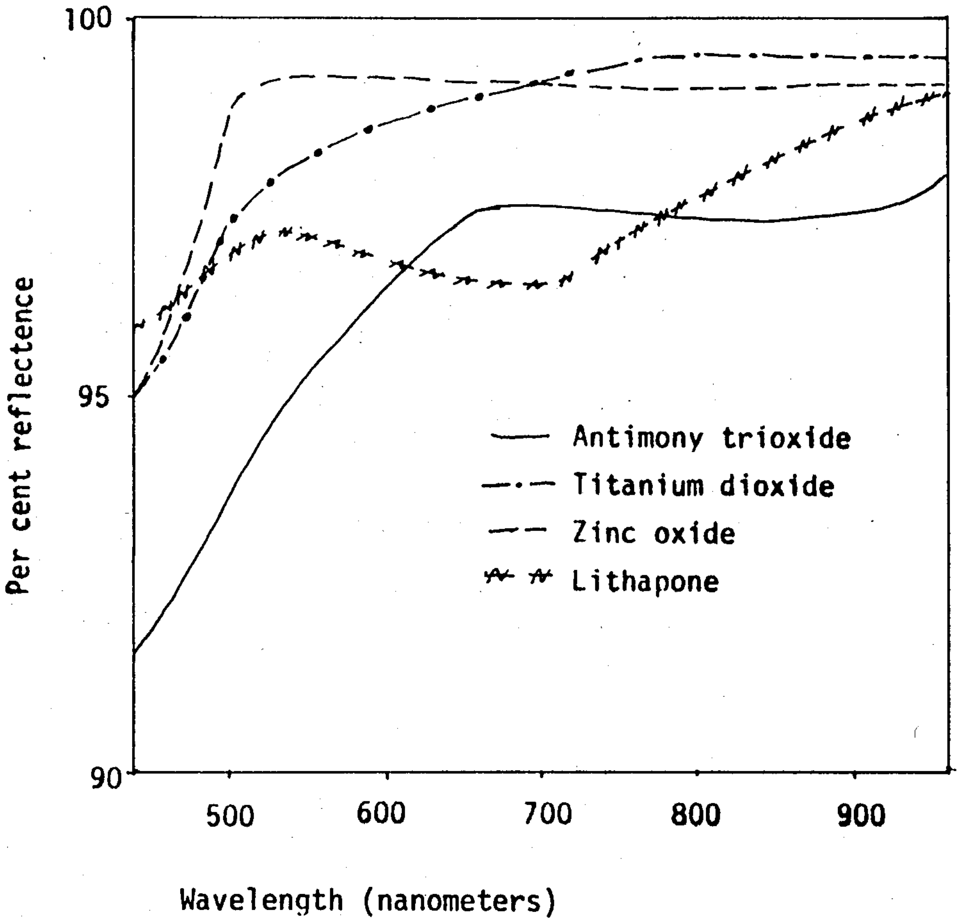
Tinting strength, a term used by Americans, and staining resistance, used by British, are synonymus terms applied to white pigments as resistance to be colored or strength of retention of color against other colorants. For a choice of pigment, consistency of tinting strength is important for a given formulation. It is expressed by a number or percentage followed by the method used in its determination.

Pigments also control the aging properties of paint surfaces. There are different ways in which paints fail and pigments have different contributions in these failures. Common paint failures are discoloration, chalking, checking, cracking, flaking, and mildew collection. Discoloration is an alternation in the original color of a paint film such as yellowing darkening fading. Chalking is a phenomenon of coating manifest by the presence of loose powder evolved from the film itself or just beneath the surface. Checking is a phenomenon in film such as breaks in the surface of the paint film, so that underlying coat is visible. Cracking is break extention through the surface of paint. Flaking is actual detachment of pieces of film. Mildew collection is attributed to the presence of mold or fungus of a type known as mildew.

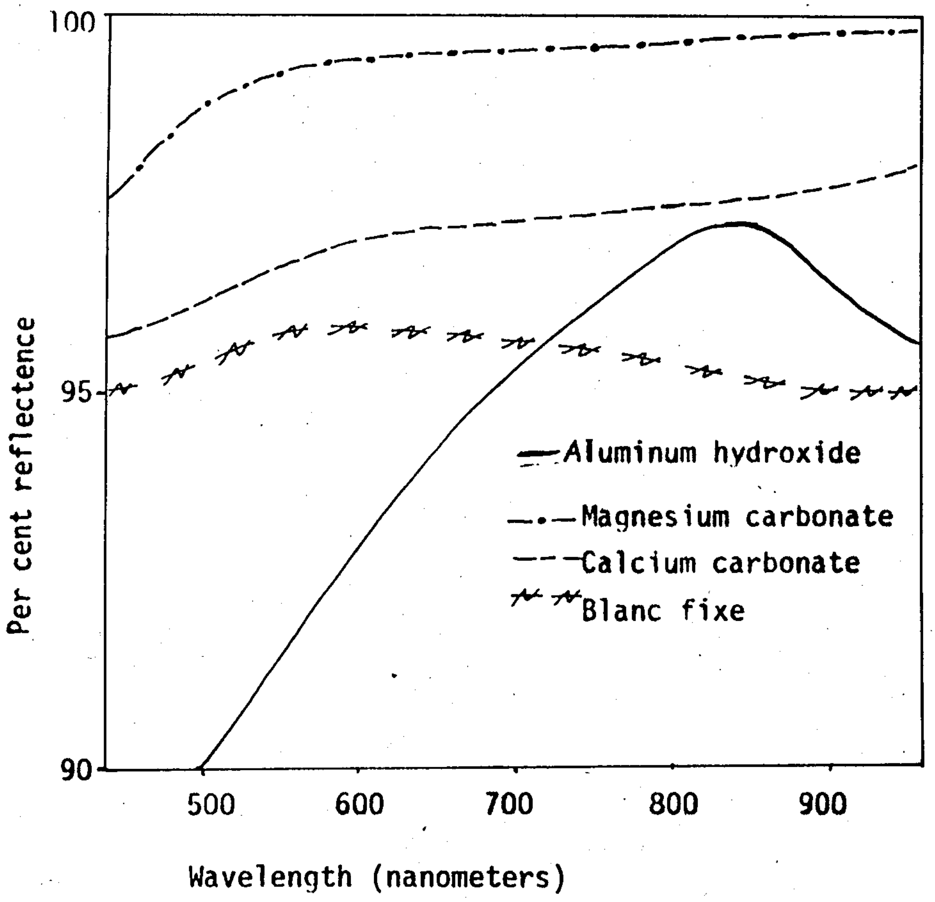
3. Antimony Trioxide as Pigment in Surface Coatings

a) Spectral Characteristics

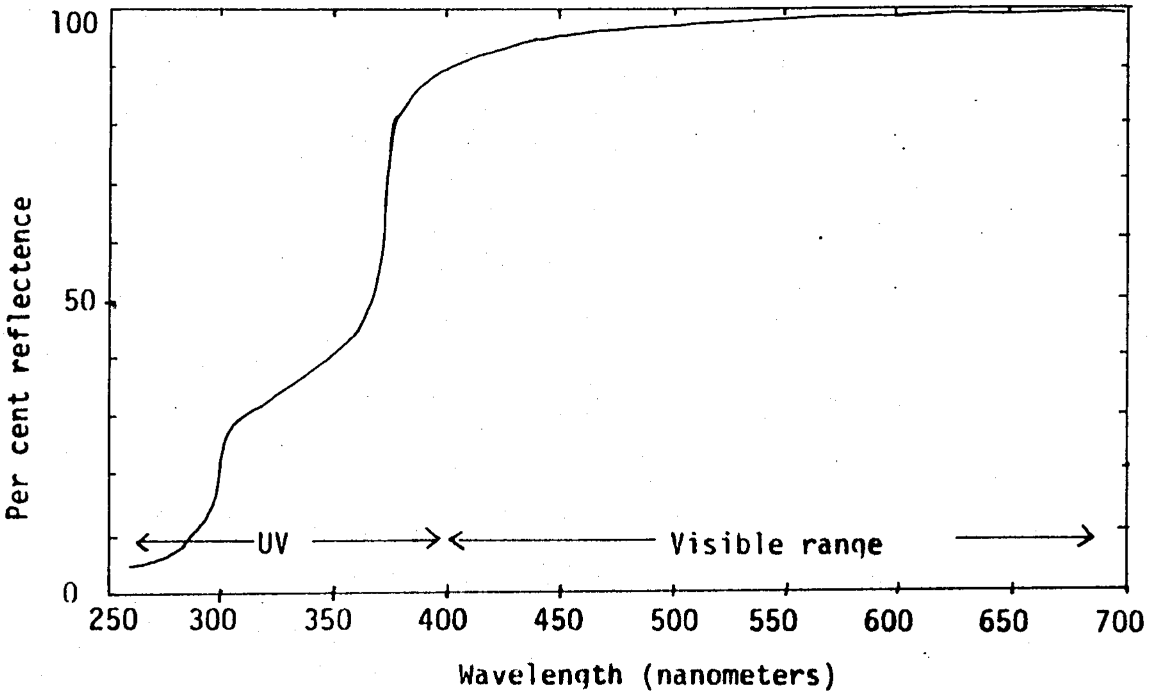
Spectral characteristics of various white pigments and extenders, zinc oxide, lithopone, anatase and rutile titanium dioxide, antimony trioxide, precipitated calcium and magnesium carbonate are shown in Graph 2 and Graph 3, Figures 186-193 in Mattiello (Mattiello, 1950). No information has been given on the grade of materials used in testing. Spectral reflectance curve for a commercial grade of a pigment antimony trioxide (Red Star/NL) of 99 percent purity (Complete analysis is in Appendix B) in near UV and visible spectrum are given in Graph 4. 100 percentage reflectence in this graph is based on magnesium oxide (Gloger, et.al., 1973). The absorptivity in short wavelengths indicates protective properties against ultraviolet light.



Graph 2 Spectral characteristics of various white pigments



Graph 3 Spectral characteristics of various extenders



Graph 4   Spectral reflectence curve for Red Star/NL

b) Hiding Power of Antimony Trioxide

Considering particle size and index of refraction, antimony trioxide has advantages. Particle size of cubic (senarmonite orthorhombic) crystals of antimony trioxide are ideal for pigment purposes. Usually the method of manufacture determines the particle size of this pigment. Products of different manufacturers and grades have different particle sizes (Appendix B). Pigments with average diameter of 1 micron are most common. According to Equations 4.1 and 4.2, the optimum size for antimony trioxide (index of refraction n_p = 2.09) in linseed oil (n_b = 1.48) measured in sodium D line (λ = 589 nanometers) is calculated to be 354 nanometers. Products of antimony trioxide with average particle sizes less than 1 micron are also available. Particle sizes of antimony trioxide manufactured from volatilization processes can be controlled with the rate of quenching of vapors to low temperatures. Pigments manufactured from hydrolysis of antimony trifloride in basic solutions are reported to be not superior to volatilized products.

There are various reports on index of refraction of antimony trioxide. A collection of reports are listed in Table 4.

TABLE 4 - Reported Indices of Refraction of Pigment Sb_2O_3 With Respect to Air.

n_p	
2.09	(Nylen, 1965)
2.20	(Price, 1943)
2.20	(Riker, 1933)
2.09-2.29	(Mattiello, 1950)
2.087-2.35	(Friedberg, 1981)
2.6	(Parmelee, 1973)

Indices of refraction of some pigments and vehicles are listed in Table 4 (Nylen, 1965).

Hiding power of antimony trioxide is greater than those of protective pigments such as zinc oxide and white lead and lie in the range of purely opacifier pigments. The hiding power is less than that of zinc sulfide or TiO_2.

TABLE 5 - Indices of Refraction for Some Pigments Binders and Air valid for Sodium D Line at Room Temperature

Pigment	n_p	Binder	n_b
TiO_2, rutile	2.76	Linseed oil	1.48
TiO_2, anatase	2.55	Tung oil	1.52
ZnS	2.37		
Sb_2O_3	2.09	Ester gum	1.50
ZnO	2.02	Phenolic resin	1.56-1.70
Basic lead carbonate	1.65		
Cobalt aluminate	1.63	Alkyd	1.50-1.60
Ultramarine	1.50-1.54	Vinyl resin	1.5
Barytes	1.64	Nitrocellulose	1.5
Whiting	1.60	Natural resin	1.5-1.55
Mica	1.60		
Silica	1.55	Air	1.0003

c) Other Properties of Antimony Trioxide Pigment

One of the most pronounced qualities of antimony trioxide as a pigment is its ease of incorporation in paint media. It is one of the few pigments which can be incorporated directly into the oil medium by "bucket and stick" methods, i.e., by simply stirring the pigment into oil. Although such methods are not now likely to be employed, only the minimum of milling is necessary for incorporation of the pigment into an oil paint system.

The oil absorption of antimony oxide is low and lies between that of white lead but lower than other white pigments. Thus the oxide is well adapted to formulations requiring high pigment concentrations. There can be variations in oil absorption of poor grades of antimony oxide. Oil absorption for good grades are fairly stable (Riker, 1933).

Antimony trioxide has an amphoteric character however it is not considered as a reactive pigment (Martens, 1968).

Paints pigmented with antimony trioxide tend to yellow in an atmosphere containing H_2S. However this could be prevented with the addition of five percent of zinc oxide. Zinc oxide reacts with H_2S to form zinc sulfide which is also white (Price, 1943).

Antimony oxide of good fineness and texture remains in suspension unusually well when formulated into paints. In a test in linseed oil batches which contained 30 to 100 percent of oxide very little settled after twelve months. Observations showed that no important "caking" took place. Antimony oxide paints have distinctive advantages for shelf goods and similar products.

Paint and enamel films containing the proper portion of antimony oxide have a very good smoothness and gloss (Riker, 1933).

Antimony trioxide pigment is designated as

C.I. 77 052 or C.I. Pigment White 11 in Colour Index (Colour Index, 1956). Various countries have specifications for pigment grade antimony trioxide. Examples are:

U.S. Federal Standard TT-A-566 (Oct, 1952), TT-P-325A (June 19, 1962), MIL-E-17970C, MIL-P-15144A, British Standards BS 239: 1952, BS 338: 1952, Australia K 50, Netherlands V 1337, N 1942, N 1552, India IS 38, Italy UNI 3 270 12.52.

Federal Standard FS TT-P-325A requires following

Sb_2O_3 percent minimum 98.0
moisture at 105°C maximum 0.5
water soluble material maximum 0.75 (Hartford, 1968).

Presence of antimony tetroxide Sb_2O_4 sometimes imparts a yellow tint to the pigment. Its presence is known when antimony trioxide is dissolved in tartaric acid leaving insoluble antimony tetroxide (Riker, 1933).

Antimony trioxide has an unusually slow and uniform rate of chalking and is one of the best pigments in resistance to cracking. With this property it is added into paints along with other pigments which have negative contribution to durability of resulting films. The chalking property of antimony trioxide pigmented coatings do not become dirty or do not discolor rapidly. Chalking does not induce reduction in protective qualities. Moderate chalking is the least serious paint failure and the most economic for repainting (Hess, 1965).

d) Use of Pigment Antimony Trioxide in Turkey

One disadvantage of antimony trioxide is its high price. This has been serious enough to curtail its use in the pigment market to low proportions. The price of antimony oxide pigments are directly effected by the cost of its raw materials. Today with a price of $ 4/kg FOB it is at least twice as expensive as titanium dioxide. Antimony trioxide is imported and used in very small quantities for pigment use in surface coatings in Turkey. One small company Boyman Boya ve Kimya San. ve Tic. A.Ş. imports yearly 500 kg of antimony trioxide to be used in marine paints in which they are specialized in. Other paint manufacturers could be buying antimony trioxide too, but the total amount of surface coating bound antimony trioxide should not exceed 1 ton per year in Turkey.

In the U.S. only a very small decreasing fraction of antimony trioxide is used in paints. The use of this material as pigment in much higher in Britain. In a book compiling 415 different paint formulations not a single usage of antimony trioxide has been encountered (Flick, 1977). Pigment antimony trioxide finds application where fire retarding coatings are needed.

4. Naples' Yellow, Nickel Antimony Titanium Yellow and Crome Antimony Titanium Buff

Naples' yellow is a basic antimonate of lead: $Pb_3(SbO_4)_2$ which is used as a paint pigment and by the ceramist as a low-temperature ingradient in glazes. In laboratory it can be obtained as a white curdy precipitate by treating a solution of potassium antimonate with lead nitrate. The precipitate turns yellow and gives off water when heated. In practice Naples' yellow (or gialliolino) is produced by igniting, in a fireclay crucuible for two hours, a mixture of tartar emetic (See page 97), with twice its weight of lead nitrate, and four times its weight of sodium chloride. The cold mass is lixiviated with water. If the temperature of fusion has been too high, the product remains as a hard mass when treated with water, otherwise it disintigrades to a fine powder. The lower the temperature of preparation the lighter the tint of the product. Too much lead oxide increases shade to a dull tint. Commercial Naples' yellow is graded into about six shades of color ranging from pale greenish yellow to a pale orange color with a pink tinge. There are many other recipes. The simplest method is to mix antimony oxide and lead oxide until it has acquired the desired tint. When ground with oil it is used in paint; and the pigment is largely used for producing yellow enamels and in glass painting. Hydrochloric acid and nitric acid slowly acts on Naples' yellow forming a colorless solution (Bannister, 1945; Mellor, 1957; Parmelee, 1973). It is designated as CI 77588, CI Pigment yellow 41 and also CI 77589, CI Pigment yellow 41 (Colour Index, 1956).

Nickel antimony titanium yellow $(Ti, Ni, Sb)O_2$ and chrome antimony titanium buff $(Ti,Cr,Sb)O_2$ are two synthetic mixed metal oxides used as pigments. Heat treatment is necessary for their manufacture. Rutile titanium dioxide acts as a host lattice for the yellow colorant formed from antimony and nickel oxides at 980°C. Chrome antimony buff is another rutile type; under high heat, ions of chemical compounds are added as dopents and diffuse into the host matrix. These pigments are not stable over 1000°C. Thus they can not be used in glazes, but they are used in vitreous enamel and plastics. Nickel antimony titanium yellow is incorporated in house-paint formulations, automative finishes and coatings for metal and plastic sidings. In siding applications, it chalks in the pigment color. Nickel antimony titanium yellow has a specific gravity of 4.3, an oil absorption of 13 grams/ 100 grams of oil and an avarge particle size of 1 micrometer (Schiek, 1981).

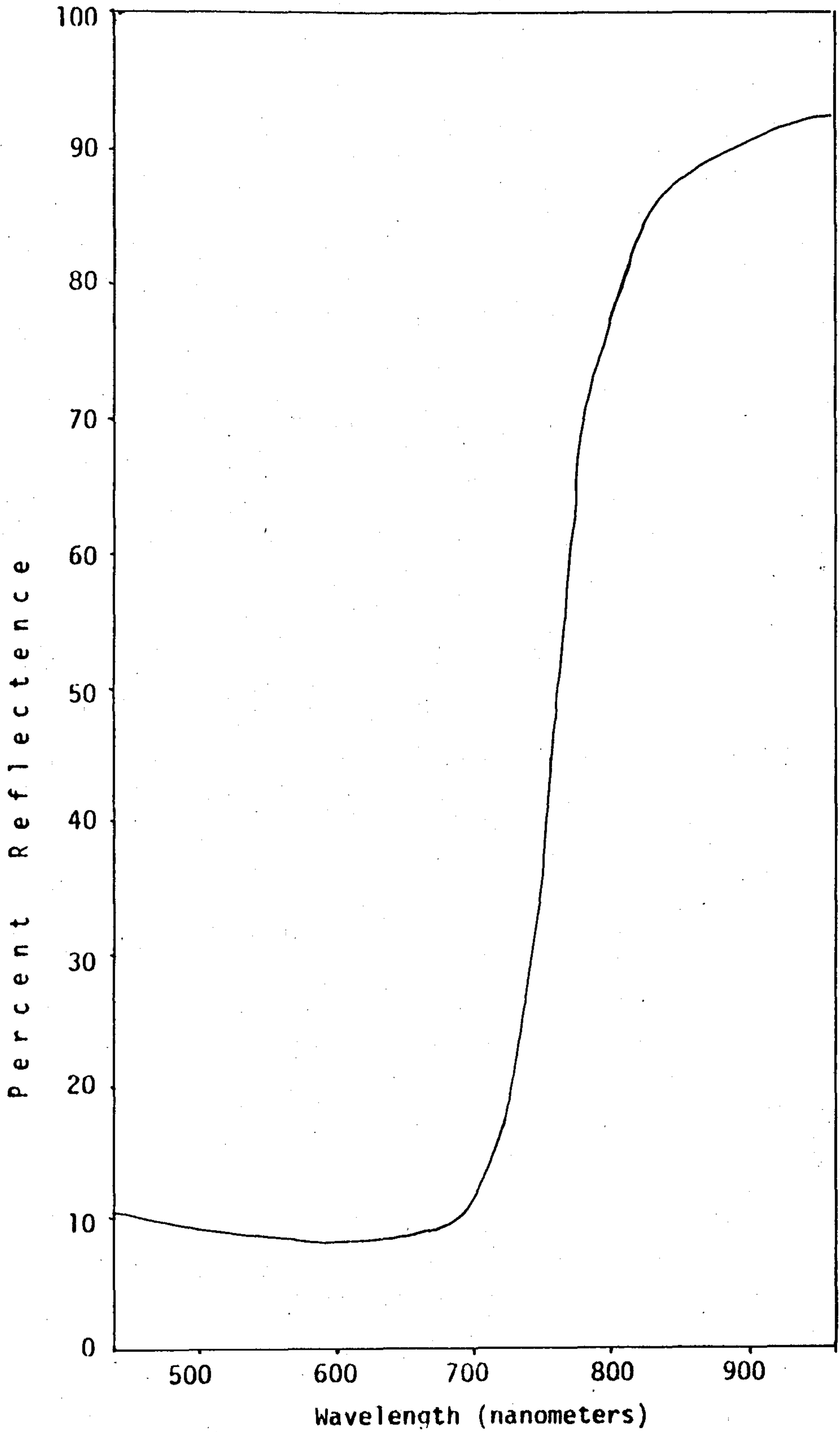
5. Antimony Trisulfide

Antimony trisulfide can be made in various colors ranging from yellow, orange to dark crimson red in amorphous form and crystalline black. Amorphous antimony trisulfide can be made by precipitating it from a solution of $SbCl_3$ with H_2S or sodium thiosulfate at over 30°C or by calcium thiosulfate. Sodium thiosulfate can precipitate antimony trisulfide from any soluble trivalent antimony salt

$$SbCl_3(aq) + 9Na_2S_2O_3(aq) \rightarrow Sb_2S_3\downarrow + 4Na_2S_4O_6 + 3Na_2SO_3 + 6NaCl$$

(Mellor, 1957)

The colour - orange to dark red - depends on the temperature and on the concentration of the solution. The amorphous form is converted to black crystalline form when heated beyond 200°C in a nonoxidable atmosphere. Under 200°C the change of color is reversible. Black antimony trisulfide is also available as liquated stibnite or crudum. Spectral characteristics of black antimony trisulfide is shown in Graph 5. In color index it is designated as CI Pigment Red 107 or



Graph 5 Spectral reflectence curve for precipitated black antimony sulfide

CI 77060 (Color Index, 1956). The compound is used as a pigment in artists colour or in camouflage paints.

Camouflage paints, which are intended to be applied either on an object itself, or to materials for covering objects which are to be disguised, require not only the reflection of visible light in the same way as the natural surroundings which it is imitating, but also reflection in the infrared region (700 to 900 nanometers) in the same way too. This requirement became necessary during the Second World War since it had been possible to photograph entirely in infrared radiation during 1930. The main problem arises in connection with natural vegetation as the chlorophyl which is the colouring matter in almost all land plants is a very good reflector of infrared light, while majority of green colors absorb strongly in infrared region appearing black in infrared photography. The only green pigment suitable for camouflage is chromium oxide green, while antimony trisulfide is good in imitating yellow (Nylen, 1965). Yellow antimony trisulfide can be obtained by precipitation from very dilute solutions resulting in small particle sizes (Mellor, 1957).

Crimson antimony sulfide is Sb_2S_3 with free sulfur and Sb_2S_4. It is due to this pigment or antimony pentasulfide that in old times red-hot-water bottles and red rubber bands showed excellent keeping (non-oxidative) qualities, against other rubber goods. So common and so good were these articles that many people thought that rubber was always red. Nowadays very little "crimson antimony" is used but since people had been so used to the good aging qualities of the articles manufactured by its use, similar articles are made containing a red dye to imitate the color and an organic antioxidant to assure proper aging (Fisher, 1941).

Today black antimony trisulfide (ground crudum) is imported at a rate of 3.5 to 4 tons per year to be used in the manufacture of rubber breaks in the automative industry. It is reported that its addition imparts lubrication in rubber. The imported material costs 2500 TL/kg and needs no elaborate specification (Gözen, 1985).

6. Antimony Pentasulfide

Sb_2S_5 is prepared by reacting a solution of sodium thioantimuanate (Schlippe's salt $Na_3SbS_4.9H_2O$) with an acid such as sulfuric or hydrochloric. The precipitate is collected and dried and is used in vulcanization and pigmentation of rubber to red. It is still used for this purpose in the U.S. Schlippe's salt is most easily prepared by dissolving stibnite or antimony trisulfide with sodium polysulfide in an aqueous media followed by filtration and crystallization. Other methods are also available such as boiling trisulfide with potash and ground sulfur filtering and if necessary crystallizing. The composition of antimony pentasulfide is variable, always containing free sulfur decomposed from the pentasulfide. No specifications are available since it is obtainable only as a crude material. Known also as golden antimony sulphide CI 77061 (Colour Index, 1956). Golden antimony sulfide may contain free sulfur and sometimes cadmium sulfate, to impart a color of red-orange type.

7. Antimony Black

Metallic antimony powder is used to impart plaster of paris an appearance of polished steel. It is made by displacing antimony in a solution of antimony trichloride with metallic zinc or iron. It is also known as Iron black CI 77050 (Colur Index, 1956).

Antimony trichloride is used as a "bronzing solution" especially for gun-barrels. For this purpose a saturated solution is mixed with olive oil, rubbed over the warmed metal and exposed to the air until the proper colour is produced. When bronzed, the metal is polished with a burnisher or wax, or coated with a natural varnish (Bannister, 1945). Antimony trichloride is designated as CI 77056 in the Colour Index (Colour Index, 1956).

The manufacture of Naples' yellow, amorphous antimony trisulfide and antimony black can all be made from metal bound antimony trioxide produced by antimony smelters like Mutlu A.Ş. Antimony pentasulfide can be made from stibnite concentrates.

B. FIRE RETARDANT ANTIMONIAL COMPOUNDS

1. Fire Retardance

Fire retardancy, flame retardancy, self-extinguishing and non-burning properties are similar terms with slight differences in their meanings. Fire retardancy and flame retardancy are commonly used to cover both the quality of retardancy and the act of retardation of the flame or fire. Flame retardance is sometimes used for materials which immediately self-extinguish after the removal of the flame under a given set of test conditions.

A coherent theory of fire retardancy has not been evolved. However a considerable body of empirical observation has been accumulated some of which are as follows.

1. The incorporation of halogen atoms into an organic composition either as an additive or as a part of a polymer structure decreases flamability and increases fire retardancy. The efficiency of halogens increase from fluorine to bromine and halogenated aromatic structures are less efficient than halogenated aliphatic hydrocarbons.
2. A combination of antimony oxide and halogen is more efficient than either alone.
3. Some combinations of phosphorous and halogens exhibit synergism.
4. Many fire retardant compositions leave large amounts of charred difficulty combustible residues when exposed to a flame (Hindersinn, 1971).

The essential requirements for cosbustion are heat, fuel and oxygen, and elimination of one of these restricts combustion. It is believed that many of the phosphorous based flame retardants operate as a solid phase inhibitor, shielding combustible material from oxygen. Halogens are believed to operate as a gas phase inhibitor. Halogens from hydrogen halides which act as a source of stoppers for free radical chains or free radicals. Antimony halides are believed to take role in the production of hydrogen halides. Since antimony halides cannot be incorporated into materials, halogens are added as a part of organic constituents and antimony as antimony oxides or sulfides (Technical Memorandum No. 1, nd).

2. Use of Antimonial Fire Retardants

The potential of antimony trioxide is in its use as a fire retardant chemical. This use accounts for 70 percent of uses of antimony oxides. The use of antimony trioxide as a fire retarding additive extends to include paints, plastics, rubber and to some extent in flame retardant fabrics paper and other building materials. The potential in some of these fields however is not clear. For example antimony trioxide tends to stiffen some fabrics making little headway in use in apparel markets. It is possible that stiffness be eliminated with new formulations (Rivoire, 1973). Also antimony trioxide is used as an ingradient on apparel to serve in increase of permanence of other effects imparted by other chemicals. In Turkey antimony trioxide is not used for either purpose in textile industry (Kaya, 1986).

In the U.S. antimony trioxide is generally marketed as fire retardant. In the U.K. antimony trisulfides are also recommended for this use. No specifications or preference on purity and physical form of antimony oxide or sulfide are available for use as fire retarding additives, except perhaps paint industry where antimony trioxide could also be required as an opacifier. In some plastics where fire retardancy but no opacity is required, antimony oxides with large particle sizes are preferred - 10 to 20 microns (U.S. Pat. 3 330 623, 1967). In 1959 a composite antimony oxide silica pigment has been patented (for use as flame retarding additive in plastics) to contain a mixture of antimony trioxide, tetroxide on silica thus reducing the cost per unit when compared with the cost of pure antimony trioxide (U.S. Pat. 2882 178, 1959). For any fire retarding quality to be imparted metal bound antimony trioxide could be of use. Where antimony trisulfide is applicable, crudum (liquated stibnite) ground to proper mesh such as below 150 microns should be suitable.

Formulations for some fire retardant paints and rubbers are given in Appendix C and Appendix D, respectively. Paints are added antimony trioxide in a range of 4 to 24 percent. However coatings which contain antimony trioxide but not containing any halogenated additive will not possess fire retarding properties. In rubber antimony trioxide can be added to make 5 to 20 percent of the bulk excluding halogenated additives. Incorporation of fire retarding additives in rubber or plastics could result in decrease in the mechanical strengths of the products.

In Turkey antimonial compounds are not used extensively for fire retardency. This is most possibly due to the lack of legal requirements for fire retardant articles. Some firms however import antimony trioxide in small quantities for fire retardant article manufacture to meet specifications on products which they manufacture. One firm, AN-KA Kablolari Sanayi ve Tic. A.Ş. imports antimony trioxide for use as fire retarding agent in cable insulation at an annual rate of 300 kilograms. The use of antimony trioxide could grow for fire retarding applications in Turkey.

In textiles antimony pentoxide can also be used as a fire retardant (Windholz, 1976).

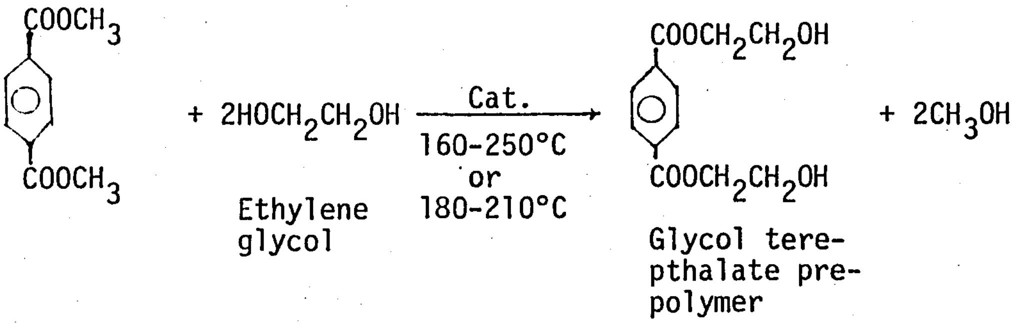
It is learned that in 1983 the Çanakkale Sümerbank Synthetic Leather Factory has imported a single batch of 35 tons of antimony trioxide most probably to be used as a fire retarding additive. However this has not been repeated yet.

C. ANTIMONIAL CATALYSTS

1. Antimony Trioxide

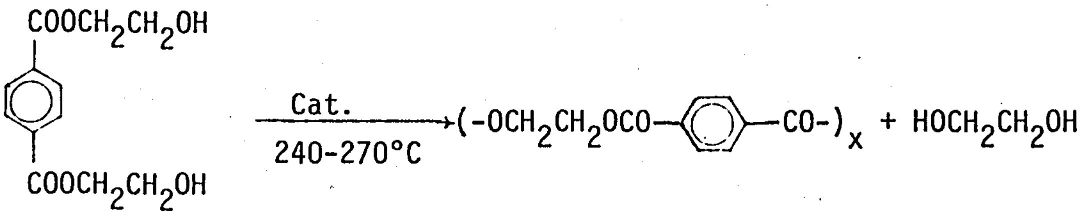
Antimony trioxide is an important catalyst used in the manufacture of some polyesters and especially in the manufacture of polyethylene terephthalate (PET). Polyester formation is the reaction of multifunctional alcohols and carboxylic acids to form linear or three dimensional polymers.

The process of polymerization is usually done in two stages. Considering the manufacture of PET, in the first stage a metal oxide or acetate (Sb_2O_3 or $Ca(OCOCH_3)_2$) is used for the formation of a prepolymer. The starting materials are dimethyl terephthalate (DMT) or terephthalic acid (TPA) and ethylene glycol.



For a continuous process a series of CSTR's are used. The older batch process simply uses the catalyzed exchange reaction between DMT and excess glycol to give a mixture the prepolymer (or β-hydroxyethyl terephthalate monomer), a very-low-molecular weight polymer and methyl alcohol. The reaction product is distilled for methanol at around 150°C. And later for excess glycol.

The prepolymer thus obtained is polymerized in a second reactor where again antimony trioxide or a titanium compound such as tetraisopropyl titanate - $Ti(OC_3H_7)_4$ - is used.



prepolymer PET polymer ethylene glycol

For a continuous system the reaction is carried out again in a series of CSTR's starting from 240°C and ending at 290°C under vacuum. In a batch process, heating is done between 240 to 270°C in carefully controlled agitation and progressively reduction of pressure to about 1.5 mm Hg. The excess glycol is removed at about 280°C. Heating is continued at this temperature until the desired degree of condensation is obtained. The increase in viscosity causing an increase in power input is used as an indicator for the degree of polymerization. It is said that SbF_3 can also be used instead of Sb_2O_3 enabling even lower temperatures. The catalysts are left in the product.

Antimony trioxide can also be used in the esterification of glycolic acid in the manufacture of ethylene glycol (Simonds, 1967; Mark, 1971; Thomas, 1970; Radriguez, 1970).

In Turkey 30 tons of antimony trioxide is imported for use in manufacture of PET in SASA A.Ş. annually since 1970. Of this half was used in continuous and half was used in batch processes. At the end of 1985 the FOB price of this catalyst has been $ 3.65/kg imported from manufacturers of Central Europe. Specifications for antimony trioxide required by SASA factory is listed in Appendix E and analysis of a commercial catalyst in Appendix B as "Blue star".

2. Antimony Tetroxide

Antimony tetroxide is claimed to find use as an oxidation catalyst, particularly for oxidative dehydrogenation of olefins (Doek, et.al.,1981).

3. Antimony Chlorides

Production of fluorocarbons by direct fluorination or hydrofluorination is reported not to be a practicable process and commercial production depends on halogen exchange through the action of hydrogen fluoride on suitable chlorocarbon using a catalyst like $SbCl_3$ or $SbCl_5$. The most important of the fluorocarbons are monofluorotrichloromethane and difluorochloromethane followed by others most of which are known as "Freons".

Three different processes are encountered in literature. The first uses antimony trichloride in a range of pressures between 10 to 20 atmospheres at a temperature of about 100°C (Gait, 1967). A second process uses $SbCl_5$ at 80°C and at seven atmospheres (Clark, et.al., 1975). A third process uses $SbCl_5$ at 65 to 90°C at atmospheric pressure (Brennan, 1965; Shrere, 1977). The first process uses little Cl_2 gas dissolved in the catalyst and the third uses addition of Cl_2 gas along the reactants. It should be noted that $SbCl_5$ starts to decompose above 70°C under atmospheric pressure, and Cl_2 dissolves in trichloride to form pentachloride.

Starting from carbon tetrachloride

$$CCl_4 + HF \xrightarrow{SbCl_5} CFCl_3 + HCl$$

$$CCl_4 + 2HF \xrightarrow{SbCl_5} CCl_2F_2 + 2HCl$$

or starting from chloroform

$$CHCl_3 + 2HF \xrightarrow{SbCl_5} CHClF_2 + HCl$$

can be obtained. All of the reactions are endothermic. Reaction is carried in a vessel in which reactants are blown through a liquid catalyst.

A trivial use of antimony trichloride is as a catalyst support for anhydrous aluminum chloride. This catalyst bed is used in liquid state for the isomerization of parafin hydrocarbons in a CSTR. For butane isomerization, typical conditions are 80-90°C and 20 atmospheres (Thomas, 1970).

Another use of antimony trichloride as a catalyst besides $BiCl_3$ at 120-200°C is in addition of HCl to ethylene. $SbCl_3$ can also catalyze addition of HCl to propylene at room temperature (Thomas, 1970).

Antimony trioxide is also used in production of ploypropylene (Carapella, 1986). Antimony trifloride is used in polymerization of aldehydes $(CH_2O)_3$ in 120-180°C (Mark, 1971).

D. ANTIMONIAL COMPOUNDS FOR GLASS AND GLAZES

1. Glasses

The ability to form glasses decreases markedly in the order of increasing size of cation of elements under nitrogen group. Vitreous As_2O_3 is well-known and is easily prepared by condensing the oxide vapors on a cold surface. Pure Sb_2O_3 can also be made only however by rapid quenching of small quantities of the melt. Sb_2O_3 can form glasses without other oxides while Bi_2O_3 can form oxides only with other oxides. Little information is available on glasses made by Sb_2O_3 (Rawson, 1967).

Antimony trioxide is rarely used as a major component in glass mixtures. One particular example of a glass with 20 percent antimony trioxide is given in Table 6. Mixed with suitable stabilizers, antimony oxide glass exhibits superior light transmitting ability near the infrared end of the spectrum. With sufficient coloring additives glass can be made opaque to all visible light except long infrared rays (Callaway, 1971).

TABLE 6 - Flint Glass (n_D = 1.5159) Composition (Scholes, 1935)

SiO_2	53.5
Bi_2O_3	20.0
K_2O	6.5
Sb_2O_3	20.0

for telescopes as obtained from Zschimmer, in Doelter's "Handbuch der Mineral Chemie", Vol. I, pp. 869-89, T. Steinkopff Dresden, 1914.

Other glasses containing minor amounts of Sb_2O_3 such as 0.2 - 2.0 percent serve most probably as chemical decolorizer or finning agent during manufacture. It is the experience of many glass makers that antimony trioxide acts contrariwise and that larger quantities of manganese dioxide (another decolorizer) is required when antimony trioxide is used in the batch (Scholes, 1935).

Antimony trioxide is most often incorporated into glass mixtures in the form of sodium meta-antimonate. Sodium antimonate, ($2NaSbO_3.7H_2O$) contains 84 to 87 percent of sodium meta-antimonate and is used successively as an opacifier in glasses and enamels (Parmelee, 1973). Antimony trioxide can be used to manufacture opal glasses which are translucent and do not directly transmit light. In such glasses opacifiers have 0.4 to 1.3 microns of diameter. The cause of translucency is the separation and suspension of minute crystals of antimony trioxide (Scholes, 1935; Shreve, 1977).

Chalcogenide Glasses

Chalcogenide glasses are based on the elements sulfur, selenium and tellerium. With oxygen only two types of oxides can be made with antimony, namely trioxide and pentoxide, while with sulfur continuous compositions are possible.

In general the normal oxide based optical glasses do not transmit beyond 3 to 5 microns because of the strong absorption of chemical bonds formed with the light chalcogen element oxygen. The first attempt to extend the wavelength range of glasses used the heavier chalcogen element sulfur. Little research is done in the subject. Most of the results have been qualitative and only a few compositions have been prepared in the amount required for quantitative evaluation. The results obtained indicate that at present Ge-As-Se is the glass that provides the best infrared optical material. The nearest alternatives for this system are Ge-Sb-Se, Si-Sb-S and Si-Sb-Se. There are only four potential suppliers of such glasses (Hilton, 1978; Rawson, 1967).

Glasses of Antimony Oxysulphides

Antimony glass or glass of antimony are made from the mixture of various antimony oxides and sulfides. They can be mixed in all proportions to form products which are also known as <u>spiessglanzglas</u> and <u>vitrum antimonii</u>. Depending on their compositions, their colors vary from yellow to dark red and black. Antimony saffron or antimony crocus is made by one part trisulfide and three parts trioxide fused together to make a glass and if necessary ground to powder (Bannister, 1945; Mellor, 1967). Antimony trisulfide is also used in the manufacture of ruby glass; glass tinted with trisulfide (Doak, et.al., 1981).

2. Glazes

Glazes are thin continuous coatings prepared from fused silicate mixtures, fusion bonded to ceramic surfaces, most commonly applied on claywares and other ceramics for protective, marking, sealing and decorative purposes. Antimony trioxide is one of the materials used in the opacification of glazes. White deeply opague-glazes are sometimes called enamels. In coating ceramic materials antimony trioxide and Naples' yellow can be used with different techniques to form overglazes, underglazes, stains or frits. All glazes containing antimony trioxide are fired at temperatures below 1000°C (Parmelee, 1973).

Antimony trioxide is rarely used by Turkish ceramists. Gorbon Işil, a ceramist company consumes it at a rate of one kilogram per year. Ege Kimya imports antimony trioxide at a rate of 300 kilograms per year for use in manufacture of frits, much less than the amount of titanium dioxide they import.

E. MATCHES, PYROTECHNICS AND EXPLOSIVE PRIMERS

1. Matches

Matches are short pieces of wood or other material at the end of which has been placed a substance that can be ignited by friction.

Safety matches involve two compositions, one at the end of a stick and one on the surface to be stricken. One of the components of the stick composition has usually been phosphorous sesquisulfide (P_4S_3) instead of which antimony trisulfide can be used. Antimony trisulfide can also be used in the surface composition of the matches. Many match compositions utilizing antimony trisulfide can be found in the Chemical Formulary. Today use of antimony trisulfide is not so common except for a few countries like Sweden. Turkish match industry does not use antimony trisulfide.

2. Pyrotechnics

Pyrotechnics is the art and science of preparing and using fireworks, items which are used both for military and nonmilitary purposes to produce a bright light for illumination or colored lights or smoke for signaling.

Antimony trisulfide is used in different kinds of pyrotechnics. One of these, Bengal light or Bengal fire is a kind of firework producing a steady and vivid blue-colored light used for signals. Bengal signal light used at sea is a mixture of antimony trisulfide with twice its weight of sulfur and six times its weight of nitre (Mellor, 1957). Bengola or bule light is a composed of saltpeter 12 parts, sulfur two parts and antimony trisulfide one part as described in the Chemical Formulary (The Chemical Formulary, 1943).

Some fireworks also use ground metallic antimony: white fire composition Saltpeter 3 parts, sulfur one part, antimony one part and antimony trisulfide one part (The Chemical Formulary, 1943).

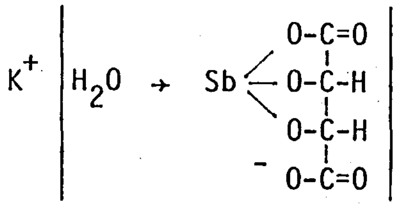
Antimony trisulfide is also used in some range finding bullets or tracer bullets which leave a white path as they travel.

3. Explosive Primers

Antimony trisulfide is also used in primer compositions along mercury fulminate or lead azide (Riegel, 1955). One composition described in the formulary is mercury fluminate 33 grams, thallium nitrate 40 grams, cobalt nitrate 10 grams and antimony trisulfide 17 grams (The Chemical Formulary, 1939).

F. OTHER ANTIMONIAL COMPOUNDS AND THEIR USES

Antimony potassium tartrate or tartar emetic



is a famous organic antimonial salt used as an emetic and as an anti-schistosomal in medicine, in some recipies for preparation of other antimonial compounds such as Naples' yellow and although outdated as a mordant in the dying of textile fibers, leather and silk by some basic dyes. The use of mordants in dyeing is now abandoned and use of tartar emetic in medicine has decreased due to its side effects. Other antimonial compounds proposed as mordants are antimony potassium oxalate, or antimony ammonium oxalate, antimony lactate, antimony tannate and antimony oxychloride. Other antimonial compounds are antimony sodium tartarate, antimony sodium thioglycollate, and antimony thioglycollamide followed by at least ten more others (Windholz, 1976).

Orthoantimonic acid H_3SbO_4 (and pyroantimonic acid) is used as a catalyst especially in the manufacture of aniline red and yellow (Mellor, 1957).

Very pure antimony compounds are useful for semiconductor applications. The most important semiconductor compounds are gallium arsenate, indium antimonide and aluminum antimonide. Also some photocells sensitive to shorter wavelengths utilize antimony. Metallic antimony is also added to fluorescent fixture linings such as calcium phosphate to produce a bule tinge phosphorence. A device called "Frigistor" utilizing the Peltier effect is used as a localized cooling apparatus consisting of alternating mixtures of bismuth telluride and antimony selenide.

V. CONCLUSION

In this work the methods of beneficiation of antimony and the production and use of its various compounds have been investigated. Turkey is a lucky country in abundance of antimonial ores, however due to the small demand of antimony and antimonial chemicals the industry that deals with manufacture of antimonial products is small. However there is a good chance for development of such industry considering the economic growth of Turkey and the demand for antimonial compounds in other countries.

Due to the fluctuative nature of antimony prices and the present saturation of the market with firms dealing with antimony, investment for the erection of new works by a new firm is risky. Investments for new works can only be done by present firms. Today firms dealing with antimony in Turkey have mostly been active in search of new antimony rich mines, mining of ores, concentration of these ores and conversion into metal. Most of the concentrate being produced in Turkey is exported. The simplest and cheapest diversification from this involvement is the production of liquated stibnite or crudum, meeting the specifications of foreign markets. A very small experimental pilot plant erected for intermittend work will at least meet the demand of crudum in Turkey. Crudum could sell about 6 tons every year in Turkey and would surely find a small but steady demand by other countries. Such a small plant accompanied with a crusher or a small grinding mill could work along an ore concentration plant or a smelting plant with low cost. The residue can be consumed easily by either of the plants.

The most beneficial activity antimony smelters could involve into would be the improvement of oxidation and volatilization plants for better product qualities, decreasing the proportion of impurities and high oxides of antimony. With better attention of operating conditions and selection of feed, products which could serve as fire retardants or chemical stocks could be produced.

For production of high grade antimony trioxide for use as catalysts and pigments, an additional small plant to a kiln producing metal bound antimony oxide to purify and refine part of the product would be sufficient. A capacity of 50 tons per year would meet the requirements of Turkey and any additional capacity could sell abroad.

The most important element in the promotion of sales of antimony oxide in Turkey is not necessarily the improvement of the product or decrease of its price but a growth in its fame. Prospective consumers seem not to be aware of the existence of antimony trioxide and its beneficial properties. The same is also true for other antimonial products such as ground crudum, trisulphide, and pentasulfide. Prospective buyers, especially of the plastics, rubber, paint, ceramic or textile industries, when given formulations or recipes containing antimonial compounds promising advantages and improvements will change their habits and even develop products of their own.

Antimonial products with uniform and consistent qualities will develop grades that will be rewarded by markets.

In the experimental section of this work antimony trioxide has been tried to be produced from stibnite and metallic antimony, since both stibnite concentrates and metallic antimony are potential starting materials in the manufacture of antimony trioxide. The apparatus used in the laboratories was makeshift and did not serve as a model for industrial furances. Any data which could have been obtained for the optimization of the operating conditions would most probably been irrelevent to these of the practiced techniques.

A repetition of the experimental work in the future should make use of sophisticated models of kilns enabling operating at higher temperatures such as 1000°C. Also a set up enabling a good control of oxygen and nitrogen ratio of the oxidizing atmosphere should be employed. Use of two seperate oxygen and nitrogen pressure tubes could be sufficient for this purpose. A better collector system such as a cyclone seperator will also be very useful in determining yield of the system.

The most thoughtful step in a study of the manufacture of a good quality antimony trioxide would be towards improvement of the operating conditions of the actual kilns rather than those of laboratory apparatus. Further study should concentrate on experimentation with one of the present installed kilns. An alternative kiln proposed according to a laboratory work can only add to the already too high capacity of present roasting kilns in Turkey.

APPENDICES

APPENDIX A

PHYSICAL PROPERTIES OF ANTIMONIAL COMPOUNDS

Vapor Pressures

Sb_2S_3 log p(in mm Hg) = 12.546 - 11200/T

T_{range} 665-809 absolute (Gmelin, 1949)

Sb_2O_3 cubic $\log_{10} p$(mm Hg) = 12.195 - 10.357/T,

T_{range} 450-557°C

orthorombic $\log_{10} p$(mm Hg) = 11.318 - 9625/T,

T_{range} 557-655°C

liquid $\log_{10} p$(mm Hg) = 5.137 - 3900/T,

T_{range} 655-900°C

(Hincke, 1930)

Sb	1	5	10	20	40	100	200	400	760 mm Hg
	886	984	1033	1084	1176	1223	1288	1364	1440 °C

(Perry, 1973)

$SbCl_3$	1	5	10	20	40	100	200	400	760 mm Hg
	49.2	71.4	85.2	100.6	117.8	143.3	165.9	192.2	220 °C

(Perry, 1973)

$SbCl_5$	1	5	10	20	40	100	200	mm Hg
	22.7	48.6	61.8	75.8	91.0	114.1	--	°C

(Perry, 1973)

	Sb_2S_3	Sb_2O_3	Sb	$SbCl_3$	$SbCl_5$
mp °C	546	656	630.5	73.4	4
bp °C	875	1570	1380	220.2	68

APPENDIX B

The terms White Star, Red Star, Green Star and Blue Star are imitation of quality designations of zinc oxide. There are similarities in the manufacture of antimony trioxide from metal antimony and the manufacture of zinc oxide manufactured from metallic zinc. The later is a method known as French process discovered much earlier (after 1751). The products of zinc oxide varied in purity as a function of distance from the oxidation furnace. Depending on qualities of products they were called, White Seal, Green Seal, Red Seal and Yellow or Blue Seal. The classification was in no way scientific and grades from different manufacturers do not necessarily correspond in color. A similar classification has also been applied for lithopone (Sward, 1944;Mattiello, 1950; Nylen, 1965; Thompson, 1960).

ANALYSIS OF AMERICAN PRODUCTS

	Standard			Premium		Special
	Regular (NL)	Red Star (NL)	Firemaster HHP,(MC)	White Star (NL)	Thermoguard S, (MT)	Duch Boy # 10 (NL)
Density (g/cm^3)	5.6	5.7	5.7	5.7	5.7	5.3
Oil absorption (lb/100 lb)	13	12	-	12	-	10
Tinting strength* Oil	190	200	-	200	-	-
Vinyl plastic	100	100	-	100	-	70
Size 325 mesh min. % through	99.9	99.95	99.9	99.95	99.9	99.2
Diameter average surface microns	1.5	1.5	1.0	1.0	1.0	2.5
Chemical analysis, wt %						
Sb_2O_3 (min)	99	99	99.75	99	99.5	99
SO_3 (max)	0.1	0.15	-	0.2	-	0.5
As (max)	0.35	0.35	-	0.1	-	0.35
Fe (max)	0.01	0.01	-	0.01	-	0.04
Pb (max)	0.15	0.15	-	0.05	-	0.25
Moisture content	0.1	0.1	-	0.1	-	0.2

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*Tinting strength - percent of standard antimony oxide (rated at 100)

(Gloger, et.al., 1973)

NC - National Lead
MC - Michigan Chemical Corp.
MT - M and T Chemicals.

ENGLISH ANTIMONY TRIOXIDE PRODUCTS

	White Star	Red Star	Green Star	Blue Star
Total Sb_2O_3	99.4	99.3	99.1	99.7
As	0.3	0.3	0.3	0.08
Cu	0.001	0.001	0.001	0.001
Fe	0.0002	0.003	0.005	0.002
Pb	0.08	0.2	0.4	0.06
Ni	0.01	0.001	0.001	0.001
H_2SO_4	0.05	0.05	0.05	0.02
Moisture	0.08	0.08	0.08	0.08
Residue on 300 mesh(%)	0.005	0.005	0.005	0.005
Average particle size (microns)	1.25	1.25	1.25	1.25

(Data Sheet 112, n.d.;Data Sheet 101, n.d)

APPENDIX C

FORMULATIONS OF FIRE RETARDANT DECORATIVE PAINTS

Alkyd based lustre finish

Sb_2O_3	6.20	percent
TiO_2	28.40	"
Cerclor65L	2.30	"
Cerclor70	7.30	"
Whiting	5.60	"
Mica	6.30	"
Long oil alkyd	25.25	
Driers.etc.	18.65	
Specific gravity	1.48	
Tack free	4-6 hrs	
Recoatable	After overnight	

Paints containing polyvinylidene

Sb_2O_3	23.4	percent
Mica	7.8	"
TiO_2	11.5	"
PVdC co-polymer	30.5	"
Thickeners bacteriostats	5.8	"
Water	21.0	"

Long Oil Alkyd - Soya oil based alkyd with oil length 67 percent and solids 57.

Cerclor 65L and Cerclor 70 are chlorinated paraffins containing 65 and 70 percent chlorine. (Timonox, 1973)

APPENDIX D

FORMULATIONS OF FIRE RETARDANT RUBBERS

Natural Rubber	
Natural polyisoprene	100
Zinc oxide	3
Stearic acid	3
Carbon black	43
Captax	1
Sulfur	3
Sb_2O_3	25
Clorinated Parafin	50

Butyl Rubber	
Isobutylene-isoprene	100
Zinc oxide	5
Stearic acid	1
Carbon black	50
Altax	1
Tellurac	1
Sulfur	1.5
Sb_2O_3	30
Clorinated Parafin	30

Neoprene	
Chloroprene	100
Neozone	2
Stearic acid	0.5
Maglite M	2
Carbon black	30
Zinc oxide	5
Sb_2O_3	15
Perchloropentacyclodecane	15

where Captax, Altax, Maglite M, Neozone, Tellurac are accelerators or antioxidants, it is the addition of the last two items that enable retardancy.

Natural Rubber: Tensile strength was reduced 50 percent while tear strength decreased 73 percent.

Butyl Rubber : All physical constants improved except tensile strength which decreased 27 percent.

Neoprene : Clorinated parafin is not compatible with neoprene physical properties exhibit loses from 20 to 54 percent.

(Trexler, 1973)

APPENDIX E

SPECIFICATION FOR PET CATALYST

Description : Sb_2O_3 Reagent grade

Use : Polymerization catalyst

Appearance : White powder free from entraneous matter

Antimony content (as Sb_2O_3): Min. 99 percent

Antimony content (as Sb) : Min. 80 percent

Moisture content : Max. 5 percent

Arsenic content (as Sa) : Max. 0.10 percent

Lead content (as Pb) : Max. 0.10 percent

Iron content (as Fe) : Max. 0.10 percent

Chlorides : Max. 0.10 percent

Sulfates : Max. 0.10 percent

Color formation : Max. 100 Hazen Units

(When 4 percent solution in pure glycol is heated to reflux) (Ergun, B., personnel communication).

Hazen method is color measurement consists of matching the tint of a liquid against a colored solution containing known amounts of cobalt chloride and potassium chloroplatinate. Procedure described in ASTM Standards 20. The Color of clear liquids, ASTM D 1209-62 states sample in Nessler tube is matched against a solution of cobalt or platinum salts in a second tube, or against standard glasses tinted to match the various Hazen numbers (Haddock, 1968).

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