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ENGINEERING AND COST STUDY OF AIR POLLUTION CONTROL
FOR THE PETROCHEMICAL INDUSTRY. VOLUME 1.
CARBON BLACK MANUFACTURE BY THE FURNACE PROCESS

AIR PRODUCTS AND CHEMICALS, INCORPORATED

PREPARED FOR
ENVIRONMENTAL PROTECTION AGENCY

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16. ABSTRACT <p>This document is one of a series prepared for the Environmental Protection Agency (EPA) to assist it in determining those petrochemical processes for which standards should be promulgated. A total of nine petrochemicals produced by twelve distinctly different processes has been selected for this type of in-depth study. Ten volumes, entitled <u>Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry</u> (EPA-450/3-73-006a through j) have been prepared.</p> <p>A combination of expert knowledge and an industry survey was used to select these processes. The industry survey has been published separately in a series of four volumes entitled <u>Survey Reports on Atmospheric Emissions from the Petrochemical Industry</u> (EPA-450/3-73-005a, b, c, and d).</p> <p>This volume covers the manufacture of carbon black by the furnace process. Included is a process and industry description, an engineering description of available emission control systems, the cost of these systems, and the financial impact of emission control on the industry. Also presented are suggested air episode procedures and plant inspection procedures.</p> <p style="text-align: right;">PRICES SUBJECT TO CHANGE</p>		
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INDUSTRY VOLUME 1:
CARBON BLACK MANUFACTURE
BY THE FURNACE PROCESS**

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Publication No. EPA-450/3-73-006-a

PETROCHEMICAL AIR POLLUTION STUDY

INTRODUCTION TO SERIES

This document is one of a series prepared for the Environmental Protection Agency (EPA) to assist it in determining those petrochemical processes for which standards should be promulgated. A total of nine petrochemicals produced by 12 distinctly different processes has been selected for this type of in-depth study. These processes are considered to be ones which might warrant standards as a result of their impact on air quality. Ten volumes, entitled Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry (EPA-450/3-73-006a through j) have been prepared.

A combination of expert knowledge and an industry survey was used to select these processes. The industry survey has been published separately in a series of four volumes entitled Survey Reports on Atmospheric Emissions from the Petrochemical Industry (EPA-450/3-73-005a, b, c and d).

The ten volumes of this series report on carbon black, acrylonitrile, ethylene dichloride, phthalic anhydride (two processes in a single volume), formaldehyde (two processes in two volumes), ethylene oxide (two processes in a single volume) high density polyethylene, polyvinyl chloride and vinyl chloride monomer.

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The study reported in this volume, by its nature, relied on the fullest cooperation of the companies engaged in the production of carbon black. Had their inputs been withheld, or valueless, the study would not have been possible or at least not as extensive as here reported. Hence, Air Products wishes to acknowledge this cooperation by listing the contributing companies.

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Continental Carbon Company
J. M. Huber Corporation
Phillips Petroleum Company
Sid Richardson Carbon Company

Additionally, Air Products wishes to acknowledge the cooperation of the member companies of the U. S. Petrochemical Industry and the Manufacturing Chemists Association for their participation in the public review of an early draft of this document. More specifically, the individuals who served on the EPA's Industry Advisory Committee are to be commended for their advice and guidance at these public meetings.

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SUMMARY

The carbon black industry has been studied to determine the extent of air pollution resulting from the operations of the various plants and processes of the industry. The purpose of the work was to provide the Environmental Protection Agency with a portion of the basic data required in order to reach a decision on the need to promulgate air emission standards for the industry.

It was concluded that the channel process for the production of carbon black is unlikely to be incorporated into a future plant design, so does not warrant consideration under new performance regulations. It was also concluded that the thermal process for the production of carbon black will, at best, achieve only a limited growth of usage so it too does not warrant consideration at this time. Consequently, the report is devoted to the study of the furnace process for the production of carbon black which is both the chief present process and the one most likely to be responsible for the future growth of the industry.

The study has revealed that the carbon black producers in the United States have made significant progress in their efforts to reduce particulate emissions from their operating plants. Historically, these plants were characterized by a black plume funneling away from the site and visible for miles. These conditions, of course, resulted in a continuous problem of sooty deposits in the surrounding communities and country side. Through the advent of new designs for bag filters and the development of new quality filter cloths, the stack exhaust from furnace black plants are now typically invisible and efficiencies of particulate removal exceed 99 percent.

However, consideration of particulates does not characterize the entire pollution potential of the industry. Being a partial oxidation process with a hydrocarbon feed, one of the major waste products is carbon monoxide, typically being emitted at a rate equal to about 1.3 pounds per pound of carbon black produced. Some United States plants have tried to eliminate this material by installing a CO-boiler and an incinerator with supplemental fuel but no heat recovery, or a plume burner but these practices are not widespread. Incinerators and waste heat boilers are reported to be in use in Europe. Furthermore, since the process feed material invariably contains small amounts of sulfur, the process also emits hydrogen sulfide and mercaptans if the CO is not further oxidized or oxides of sulfur if a combustion step is included. Oxides of nitrogen are also emitted.

As a result of this study, it was concluded that the use of bag filters is the best, demonstrated technique for control of particulate emissions from the main process vent and should be part of all future plant designs. There is little likelihood that any carbon black producer would build a new plant without bag filters, even if no governmental body required such an installation, so the inclusion of this requirement in any new source standard would not impose any additional cost on the industry.

It was further concluded that off-gas combustion is the only demonstrated technique for the control of emissions of reduced sulfur compounds and/or carbon monoxide. The technique has been demonstrated in the U.S. in only three forms, i.e., by plume burping, by means of a CO-boiler and by means of

SUMMARY (continued)

a fuel fired incinerator, although various other techniques were investigated during the course of the study and are reported to be practiced in Europe. It should be noted that none of these control methods remove sulfur but merely convert it to the oxide form and that no feasible technique has been found to remove either the reduced or oxidized form of sulfur compound. Furthermore, these control methods also produce additional oxides of nitrogen.

Therefore, assuming that oxidation of carbon monoxide and sulfur compound are the goals of new source standards, the best demonstrated technique is the plume burner, if minimum capital cost is the principal criterion of "best". However, depending on the plant, it may be necessary to provide supplemental fuel to flare the off-gas. On the other hand, the CO-boiler removes pollutants more efficiently, and recovers a substantial quantity of energy, but typically at a capital cost penalty because of the need for a stand-by unit to assure a reliable supply of process steam. If a reliable off-gas combustion device could be demonstrated (i.e., the thermal incinerator-waste heat boiler combination as assumed in the study and reported from Europe), it would clearly be the "best" and would probably result in a reduction in annual direct operating costs, even though it probably would also result in a reduction in percentage return on investment because of increased capital charges.

The actual cost to industry is difficult to estimate because of the uncertainty of the need for stand-by units and also because of the need to install steam driven equipment rather than the conventional electric motor drives that are typically used today. However, it is likely that additional capital requirements of about \$1,000,000 (1973 dollars) per combustion unit per new 90 MM pounds per year carbon black plant is the correct order of magnitude for emission control by means of off-gas combustion with energy recovery. It should be noted that the only feasible retrofit control technique is plume burning or fuel fired incineration if higher efficiencies are sought, because existing plants have no need for the potential steam that can be generated.

Several miscellaneous emission sources also exist on typical carbon black plants. These are drier vents, product transfer systems and storage systems. In each case, the use of bag filters was found to be the best demonstrated technique for emission control since the only emissions of any magnitude from these facilities are particulates. These sources of emission are almost always controlled in this manner although the installation does not normally pay for itself. However, the promulgation of new source standards to this effect would not impose additional hardship on the industry because the control is considered "standard".

It was calculated, in the course of the study, that by 1985, the carbon black industry will emit nearly seven billion pounds of pollutants per year (of which 6.5 billion pounds will be carbon monoxide) if plants continue to be designed as are the "typical" existing plants. This can be reduced to about 0.6 billion pounds per year if plume burners are installed on all existing plants and efficient off-gas combustion devices installed on all new plants. However, included in that total will be an increase of about 0.1 billion pounds per year of sulfur oxides and an increase of about five million pounds per year of nitrogen oxides. Although stack analyses are not available, the new plant emission factors can be expected to be about 0.004 pounds NO_x per pound of carbon black and 0.03 pounds of SO_x per pound of carbon black with

SUMMARY (continued)

only traces of hydrocarbon, particulates and carbon monoxide emitted if a CO-boiler or its equivalent were installed.

The capital expenditure required by the industry to effect these reductions will be about \$23,000,000 (at 1973 prices) if stand-by combustion devices are not required, and nearly \$40,000,000 if stand-by units are installed.

It was concluded that the most likely research area for reducing emissions from new carbon black plants would be the development of a system using oxygen feed to the process with partial recycle of the off-gas to control flame temperature. The industry could not justify any sulfur removal research but would probably benefit from any breakthrough in the petroleum industry's efforts to desulfurize heavy oils or in the power generating industry's efforts to desulfurize flue gas.

I. Introduction

Carbon black is manufactured by the burning of hydrocarbons in a limited supply of air. This finely divided material (100 to 4000 Å diameter) is of industrial importance primarily as a reinforcing agent for rubber. It is also used as a colorant for printing ink, paint, paper and plastics.

Three basic processes currently exist in the United States for producing carbon black. They are: the furnace process, accounting for about 89% of production; the older channel process, which accounts for less than 2% of production; and the thermal process. Atmospheric pollutants from the thermal process are small since the principal exit gases, which are rich in hydrogen, are used as fuel in the process. In contrast, the pollutants emitted from the channel process are excessive and characterized by highly visible black smoke. Emissions from the furnace process consist of water vapor, carbon dioxide, nitrogen, carbon monoxide, hydrogen, hydrocarbons, particulate matter, and some sulfur compounds.

A process description, industry survey of emission sources, effluent characteristics, control practices and equipment in addition to plant economics for the furnace process are presented in the following sections. A similar study for the thermal and channel processes was not made because of the low pollution and limited use of these respective processes.

II. Process Description and Typical Material Balance

The fundamental steps in carbon black manufacturing, by the furnace process are:

- A. Production of black from feed stock,
- B. Separation of black from the gas stream, and
- C. Final conversion of the black to a marketable product.

In the furnace process, carbon black is produced by burning a feed stock. This feed may be either light hydrocarbon gas or a mixture of gas and heavy aromatic oil. However, because of the high cost of natural gas, a mixed feed is used in most plants. This feed is preheated and injected into a reactor with a limited supply of combustion air. The flue gases and entrained carbon from the reactor (furnace) are cooled by heat exchange against reactor feed and water quench. This stream (450 to 500° F) is then sent to bag filters for carbon black recovery. The recovered carbon black is transported to a finishing area by screw or pneumatic conveyors.

In the finishing area the black is passed through a pulverizer to break up lumps. This produces a 5 to 12 lb./cu. ft. dusty product. In order to obtain a marketable material that can be transported, the carbon black is converted into pellets or beads with a 20 to 35 lbs./cu. ft. bulk density. Normally pelleting is accomplished by a wet procedure. The resulting wet product (30 to 40 wt. % water) is sent to driers. The drier product is then screened, bagged and sent to storage.

Figure CB-1 presents a block flow diagram for a typical plant and indicates the various vent streams from this unit. Particulate emissions in these vent streams are affected by the type of collection equipment used. Total volume and composition of the vent gas is largely determined by the overall yield which is influenced by the type of feed (that is, liquid or gas), the ratio of gas to oil in the feed, and the amount of combustion air.

Furnace type units with gas feed or mixed feed (high proportion of gas) produce larger amounts of carbon oxides than units operating with predominantly oil feed. This increased CO and CO₂ production means more oxygen (air) is required and, therefore, more nitrogen has to be vented.

The main petroleum streams used as feedstock include:

- A. Cracked fuel oil from thermal cracking of cycle stocks or the vacuum flash distillate from this cracked fuel oil.
- B. Thermal or catalytic cycle stocks.
- C. Aromatic extract from catalytic cycle stocks.

The best raw material especially suited for the production of modern high structure carbon blacks is highly aromatic, low sulfur, high molecular weight resins and asphaltenes, substantially free of suspended ash, carbon and water.¹ Carbon black yields from oil can generally be correlated with the aromaticity of the feed stock. The Bureau of Mines Correlation Index is an approximate indication of suitability of feed stocks. However, this analysis alone can not be used to determine feed stock quality. Actual yield can only be determined by pilot plant tests.

* IF BAG FILTER IS EMPLOYED, FILTERED GAS IS VENTED TO ATMOSPHERE.

FOR
ENVIRONMENTAL PROTECTION AGENCY
CONTRACT NO. 68-02-0255

CATALYTIC, INC.		ENGINEERING DEPT., PHILA., PENNA. 19102	
FIGURE CB-1		SIMPLIFIED FLOW DIAGRAM	
FOR		FURNACE BLACK PROCESS	
DATE	BY	REVISION	APPROVED
30 509	J. D. W.	R-242	A

FIGURE CB-1

SIMPLIFIED FLOW DIAGRAM

FOR

FURNACE BLACK PROCESS

30	509	B-242	A
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1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
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Typical carbon black yields for the various processes are as follows:

<u>Process</u>	<u>Grade* of Carbon</u>	<u>Ave. Particle Diam. A°</u>	<u>Lbs. Carbon Black per 100 lbs. of Carbon Feed</u>
Channel	ALL	90-290	5-10
Thermal			
Fine particle size	FT	1800	40-45
Medium " "	MT	4700	45-50
Furnace			
Gas Feed			
Small particle size	FF	400-500	10-15
Large " "	HMF, SRF	600-800	25-40
Oil Feed (Typicall includes some supplemental gas)			
Small particle size	SAF, ISAF, HAF	180-280	35-55
Large " "	FEF, GPF	400-550	40-65

*Industry designations, descriptive such as FT is fine thermal, SRF is semi-reinforcing furnace, GPF is general purpose furnace. The ASTM also has a complete system of designations which is too lengthy to include here.

Small particle size carbon black (SAF, ISAF and HAF) from the oil furnace process represents over half the total carbon black production.

Operating conditions such as feed composition, furnace residence time, temperature, fuel/air ratio, oil/gas ratio and quench conditions influence the properties of the carbon black product and, therefore, can not be modified appreciably for any given grade of product. Some producers indicate this also applies to operating pressure.

Table CB-1 presents a material balance in pounds per hour for an oil feed (gas and oil) furnace plant producing 30,000,000 lbs./yr. large particle (GPF) plus 60,000,000 lbs./yr. small particle (HAF) carbon black. This "Typical" or "model" unit will be used in economic studies discussed later in this report. Table CB-1A presents the same material balance with quantities expressed as tons per ton of product carbon black.

Table CB-2 presents an estimated heat balance around the furnace reactor system. It should be noted that the heat balance is influenced to large extent by the type of carbon black being produced. The presented balance is based on Table CB-1A product distribution.

TABLE CB-1
TYPICAL MATERIAL BALANCE FOR
OIL FURNACE BLACK (c)
PRODUCING 90 MM LBS./YR. CARBON BLACK

Component	1	2	3	4	5	6	7	8
	Oil Feed	Gas Feed	Air To Reactor	Process Vent	Make Up Water	Air To Drier	Combined Drier Vent	Carbon Black Product
Hydrogen								
Carbon Dioxide				1,229				
Carbon Monoxide				9,978		2,457	2,457	
Hydrogen Sulfide				14,071				
Sulfur Oxides (SO ₂)				306				
Methane				TR				
Acetylene		4,492		318				
Ethane		991		383				
Arom. Oil	17,980							
Nitrogen								
Oxygen		463	90,223	90,686		37,934	37,934	
Nitrogen Oxides (NO ₂)			27,046	810		8,016	8,016	
Carbon Black				18 (d)				
Water				24				
				80,223	76,898	1,913	10,933	11,024
LBS./HR.	17,980 (a)	5,946	117,269	198,046	76,898	50,320	59,342	11,024

CB-5

- (a) Assumed to contain 1.9 wt. % sulfur.
- (b) Miscellaneous carbon black losses equal 1 lbs./hr.
- (c) Due to timing, these data are not Industry averages but have only a single producer as the data source.
- (d) Determined by EPA Method 7.

TABLE CB-1A
TYPICAL MATERIAL BALANCE FOR
OIL FURNACE BLACK PLANT (c)

1	2	3	4	5	6	7	8	
<u>Component</u>	<u>Oil Feed</u>	<u>Gas Feed</u>	<u>Air To Reactor</u>	<u>Process Vent</u>	<u>Make Up Water</u>	<u>Air To Drier</u>	<u>Combined Drier Vent</u>	<u>Carbon Black Product</u>
Hydrogen				0.1115				
Carbon Dioxide				0.9051		0.2229	0.2229	
Carbon Monoxide				1.2765				
Hydrogen Sulfide				0.0278				
Sulfur Oxides (SO ₂)				TR				
Methane		0.4075		0.0289				
Acetylene				0.0347				
Ethane		0.0899						
Arom. Oil	1.6309							
Nitrogen		0.0420	8.1842	8.2262		3.4410	3.4410	
Oxygen			2.4534	0.0735		0.7271	0.7271	
Nitrogen Oxides (NO ₂)				0.0016 (d)				
Carbon Black				0.0021			0.0002	1.0000
Water				7.2771	6.9756	0.1735	0.9917	
Tons/Ton of Product	1.6309 (a)	0.5394	10.6376	17.9650	6.9756	4.5645	5.3829	1.0000

CB-6

CB-6

- (a) Assumed to contain 1.9 wt. % sulfur.
- (b) Miscellaneous carbon black losses equal 0.0001 tons/ton of product.
- (c) Due to timing, these data are not Industry averages but have only a single producer as the data source.
- (d) Determined by EPA Method 7.

TABLE CB-2
CARBON BLACK REACTOR SYSTEM
HEAT BALANCE (a)

Heat Out

Quench (to 500° F)	7,494	BTU/LB. of Carbon Black
Radiation Heat Losses (500° F ΔT)	2,436	" " " "
Preheater Inefficiency	572	" " " "
Incremental Effluent Heat Content (b)	<u>1,785</u>	" " " "
Total	<u>12,287</u>	" " " "

Heat In

Exothermic Heat of Reaction (c)	10,381	BTU/LB. of Carbon Black
Fuel to Feed & Air Preheaters	<u>1,906</u>	" " " "
Total	<u>12,287</u>	" " " "

NOTES:

a) Basis

- 1) Table CB-1A Material Balance.
- 2) 2600° F Reactor (furnace) outlet temperature.

b) Difference in heat content of effluent @ 500° F and feed @ 80° F plus air @ 120° F.

c) Net reaction heat is exothermic. It is made up of an exothermic combustion and an endothermic cracking reaction.

III. Manufacturing Plants and Emissions

Table CB-3A presents a list of U. S. plants currently producing carbon black by the furnace process. Most of these plants are located in Texas and Louisiana. Approximately one-third of the plants have been built in residential areas and the remainder are within 13 miles of towns with population ranging between 550 to 76,000.¹

In addition to indicating plant sizes, Table CB-3A also shows atmospheric emission data for these units.

A. Continuous Air Emissions

1. Main Process Vent Gas

This stream consists of the gross reactor effluent plus quench water after recovery of carbon black product and represents the main source of emissions from the carbon black plant. For the "typical" or "model" plant of this study, it is equivalent to about 3.5 million scfh of which nearly half is water vapor.

In most cases, the process vent gas atmospheric emissions presented in Table CB-3A are average values for producing various types of carbon black in these units. Actual vent gas composition can vary considerably from the average figures shown, depending upon the grade of carbon black being produced. The vent gas will normally contain six to 14 vol. % (dry basis) CO. However, this value can be as high as 20 vol. %. Total sulfur normally ranges between 0.02 and 0.16 vol. % with the actual quantity depending upon sulfur content of the hydrocarbon feed. Anywhere from 10 to 40% of the feed sulfur is retained in the carbon black product and the remainder is vented primarily as H₂S with trace quantities of SO₂, SO₃, thiophene, carbonyl sulfide and CS₂.

The vent gas also contains 15 to 200 ppm of NO_x, 5.5 to 15 vol. % hydrogen and 0.3 to 1.5 vol. % hydrocarbons. (See Table CB-4 for typical breakdown of components.)

In some cases, the main process vent gas stream has a slight H₂S odor at ground level. This is reported to be the only carbon black plant vent stream that has a noticeable odor.

No actual test data are available concerning size distribution of particulates in this and the other vent streams. However, it is believed that size distribution of particulates in the process vent is similar to that of the carbon black product being produced. This is because most if not all of the carbon black emitted is a result of small leaks in the product recovery bag filters.

Atmospheric emissions from the various vent streams are directly proportional to quantity of carbon black being produced. This is primarily true because the normal carbon black plant consists of

TABLE CB-3A
SUMMARY OF U. S. FURNACE BLACK PLANTS
AND ATMOSPHERIC EMISSIONS FROM THESE FACILITIES

Sheet 1 of 23

50-1

Plant Code Number	Unit Number	Capacity, Tons Carbon Black/Yr.	Average Production, Tons/Yr.	Range in Production, % of Max.	Feedstock (f) (h)
1	2	35,000	19,250	25,000	21,000 16,750
Emissions to Atmosphere					
Stream Flow (a), Lbs./Hr.					
Composition, (b) Tons/Ton Carbon Black					
Product Finishing	Drier	Process	Drier	Drier Indi-rect Heat	Drier Indi-rect Heat
8,350	22,000	97,800	18,900	Source Vent	Source Vent
Process 182,700	0.004	0.004	0.00007	Process 97,800	Process 97,800
0.004	X	X	0.00007	0.003	0.00005
X	1.554	1.554	1.197	X	X
1.597	0.010	0.010	0.007	0.011	0.019
0.010	0.003(SO _x)	0.003(SO _x)	0.002(SO _x)	0.003(SO _x)	0.005(SO _x)
0.003(SO _x)	0.072	0.069	0.053	0.074	0.130
X	X	X	X	X	X
X	X	X	X	X	X
X	X	X	X	X	X
Sample Tap Location	Calc'd	Calc'd	Calc'd	Calc'd	Calc'd
Date or Freq. of Sampling	Calc'd	Calc'd	Calc'd	Calc'd	Calc'd
Type of Analysis	Calc'd	Calc'd	Calc'd	Calc'd	Calc'd
HC, CO, CO ₂ & Inerts	Calc'd	Calc'd	Calc'd	Calc'd	Calc'd
Particulate	Calc'd	Calc'd	Calc'd	Calc'd	Calc'd
Hydrogen Sulfide	Calc'd	Calc'd	Calc'd	Calc'd	Calc'd
SO ₂	Calc'd	Calc'd	Calc'd	Calc'd	Calc'd
NO _x	Calc'd	Calc'd	Calc'd	Calc'd	Calc'd
Odor	Calc'd	Calc'd	Calc'd	Calc'd	Calc'd
Vent Stacks	Calc'd	Calc'd	Calc'd	Calc'd	Calc'd
Number	1	1	1	1	1
Height	80'	89'5"	95'	95'	150'
Diameter	2'8" x 2'3 1/2"	3'4"	3'0"	3'0"	3'1 1/2" x 1'8 1/2"
Exit Gas Temp., °F	400	400	400	400	400
SCFM Per Stack (a)	17,780	28,500	4,560	28,500	32,900
Type of Recovery System	Electrostatic Precip.	Electrostatic Precip.	Electrostatic Precip.	Electrostatic Precip.	Electrostatic Precip.
Cyclone	Calc'd	Calc'd	Calc'd	Calc'd	Calc'd
Bag Filter/Total Compartments	Calc'd	Calc'd	Calc'd	Calc'd	Calc'd
Date Installed	1970	1970	1970	1970	1970
Vacuum Clean-up	Flow, SCFM (Air)	Flow, SCFM (Air)	Flow, SCFM (Air)	Flow, SCFM (Air)	Flow, SCFM (Air)
Particulate, T/T Carbon Black	0.04	0.04	0.04	0.04	0.04
Type of Recovery, % Recov.	0.004	0.004	0.004	0.004	0.004
Stack Height/Diameter	0.003	0.003	0.003	0.003	0.003
Date Installed	1.597	1.597	1.597	1.597	1.597
Total Emissions, Ton/Ton Carbon Black	0.04	0.04	0.04	0.04	0.04
Hydrocarbons & H ₂ S (X)	0.004	0.004	0.004	0.004	0.004
Particulates	0.003	0.003	0.003	0.003	0.003
NO _x	1.597	1.597	1.597	1.597	1.597
SO _x	0.004	0.004	0.004	0.004	0.004
CO	0.003	0.003	0.003	0.003	0.003

TABLE CB-3A CONT.
SUMMARY OF U. S. FURNACE BLACK PLANTS
AND ATMOSPHERIC EMISSIONS FROM THESE FACILITIES

Sheet 2 of 23

Plant Code Number

50-2

50-3

Unit Number	1	2	1	2
Date On-stream				
Capacity, Tons Carbon Black/Yr.	13,200	13,800	17,500	16,250
Average Production, Tons/Yr.				
Range in Production, % of Max.				
Feedstock (F) (h)				
Type of Carbon Black (F)				
Emissions to Atmosphere				
Stream				
Flow (a), Lbs./Hr.				
Composition, (b) Tons/Ton Carbon Black				
Particulate	0.0007	0.00004	0.002	0.008
Carbon Dioxide	X		X	X
Carbon Monoxide	2.511		0.876	2.837
Hydrogen Sulfide	0.010		0.003	0.011
Sulfur Oxides (SO _x)	0.003 (SO _x)		0.001 (SO _x)	0.004
Hydrogen				
Methane				
Acetylene				
Nitrogen + Argon	X		X	X
Oxygen	X		X	X
Nitrogen Oxides (NO ₂)			X	X
Water	X		X	X
Sample Tap Location				
Date or Freq. of Sampling				
Type of Analysis				
HC, CO, CO ₂ & Inerts				
Particulate				
Hydrogen Sulfide				
SO ₂				
NO _x				
Odor				
Vent Stacks				
Number	1	1	1	1
Height	82'	87'	87'	165'
Diameter	5'1 3/8" x 2'10"	1'2"	1'3/4"	8'0"
Exit Gas Temp., °F	400	200	200	400
SCFM Per Stack (a)	31,550	2,020	1,675	91,100
Type of Recovery System				
Electrostatic Precip.				
Cyclone				
Bag Filter/Total Compartments	X		X	X
Other				
Date Installed				
Vacuum Clean-up				
Flow, SCFM (Air)				
Particulate, T/T Carbon Black				
Type of Recovery, % Recov.				
Stack Height/Diameter				
Date Installed				
Total Emissions, Ton/Ton Carbon Black				
Hydrocarbons & H ₂ S (x)	0.06	0.02	0.02	0.07
Particulates	0.007	0.002	0.002	0.008
NO _x	0.003	0.001	0.001	0.004
CO	2.511	0.876	0.876	2.837

CB-10

Bolometer

1,000

Bag Filter
80'/1' 3/4"

TABLE CB-3A CONT.
SUMMARY OF U. S. FURNACE BLACK PLANTS
AND ATMOSPHERIC EMISSIONS FROM THESE FACILITIES

[illegible]

TABLE CB-3A CONT.

Sheet 4 of 23

50-6

Unit Number	30,000	No seasonal variation	Residue tar
Date On-stream			
Capacity, Tons Carbon Black/Yr.			
Average Production, Tons/Yr.			
Range in Production, % of Max.			
Feedstock (f) (h)			
Type of Carbon Black (f)			
Emissions to Atmosphere			
Stream			
Flow (a), Lbs./Hr.			
Composition, (b) Tons/Ton Carbon Black			
Particulate			
Carbon Dioxide			
Carbon Monoxide			
Hydrogen Sulfide			
Sulfur Oxides (SO ₂ /SO ₃)			
Hydrogen			
Methane			
Acetylene			
Nitrogen and Argon			
Oxygen			
Nitrogen Oxides (NO ₂)			
Water			
Sample Tap Location			
Date or Freq. of Sampling			
Type of Analysis			
HC, CO, CO ₂ & Inerts			
Particulate			
Hydrogen Sulfide			
SO ₂ + SO ₃			
NO _x			
Odor			
Vent Stacks			
Number			
Height			
Diameter			
Exit Gas Temp., °F			
SCFM Per Stack (a)			
Type of Recovery System			
Electrostatic Precip.			
Cyclone			
Bag Filter/Total Compartments			
Other			
Date Installed			
Vacuum Clean-up			
Flow, SCFM (Air)			
Particulate, 1/1 Carbon Black			
Type of Recovery, % Recov.			
Stack Height/Diameter			
Date Installed			
Total Emissions, Ton/Ton Carbon Black			
Hydrocarbons & H ₂ S (x)			
Particulates			
NO _x			
SO _x + SO ₃			
CO			

TABLE CB-3A CONT.
SUMMARY OF U. S. FURNACE BLACK PLANTS
AND ATMOSPHERIC EMISSIONS FROM THESE FACILITIES

Plant Code Number									
Location									
Unit Number									
Date On-stream									
Capacity, Tons Carbon Black/Yr.									
Average Production, Tons/Yr.									
Range in Production, % of Max.									
Feedstock (f) (h)									
Type of Carbon Black (f)									
Emissions to Atmosphere									
Stream									
Flow (a), Lbs./Hr.									
Composition, (b) Tons/Ton Carbon Black									
Particulate									
Carbon Dioxide									
Carbon Monoxide									
Hydrogen Sulfide									
Sulfur Oxides (SO ₂ /SO ₃)									
Hydrogen									
Methane									
Acetylene									
Nitrogen + Argon									
Oxygen									
Nitrogen Oxides (NO ₂)									
Water									
Sample Tap Location									
Date or Freq. of Sampling									
Type of Analysis									
HC, CO, CO ₂ & Inerts									
Particulate									
Hydrogen Sulfide									
SO ₂									
NO _x									
Odor									
Vent Stacks									
Number									
Height									
Diameter									
Exit Gas Temp., °F									
SCFM Per Stack (a)									
Type of Recovery System									
Electrostatic Precip.									
Cyclone									
Bag Filter/Total Compartments									
Other									
Date Installed									
Vacuum Clean-up									
Flow, SCFH (Air)									
Particulate, T/T Carbon Black									
Type of Recovery/% Recov.									
Stack Height/Diameter									
Date Installed									
Total Emissions, Ton/Ton Carbon Black									
Hydrocarbons & H ₂ S									
Particulates									
NO _x									
SO _x									
CO									
AND ATMOSPHERIC EMISSIONS FROM THESE FACILITIES									
50-7									
99,500									
No seasonal variation									
Residuum tar									
Process	Process	Process	Process	Transport	Transport	Drier Indirect	Drier	Drier	Emergency
59,200 (m)	86,300 (m)	52,800 (m)	90,400 (m)	Gas Vent	Gas Vent	Ht. Source Vent	Purge Vent	Purge Vent	Relief
0.0002	0.0004	0.0002	0.0004	42,000	21,600	23,900	56,000	132,800 (p)	
0.455	0.664	0.406	0.695	0.00016	0.00008	X	0.00030	0.00001	X
0.022	0.032	0.020	0.034				X	X	
0.0002	0.0003	0.0001	0.0003						
0.0045	0.0065	0.0040	0.0069						
0.002	0.002	0.002	0.002						
0.0003	0.0005	0.0003	0.0006						
1.255	1.831	1.121	1.917						
0.983	1.434	0.878	1.501	X	X	X	X	X	X
Accessible				X	X	X	X	X	X
Daily (Except Sulfur & Part.)									
Orsat + G. C.									
WP - 50 (Western Precipitation) (q)									
G. C.									
G. C. & wet gas analysis									
H ₂ S (Occasionally)									
1	1	1	1	None	None	None	None	None	None
79'	79'	105'	109'	87', 79', 85'	89'	8	2	1	28
7'0"	7'0"	7'0"	10'0"	2 @ 14", 1 @ 15"	2'0"	75'	76'	75'	25'
1300	1300	1300	1300	80 - 160	80-160	2'0"	2'9"	3'0"	1'2"
16,800 (m)	24,400 (m)	15,000 (m)	25,600 (m)	3,050	4,700	600-800	400	300-400	1000-1500
						650	4500/62250	15,000	1,250
							</		

TABLE CB-3A CONT.
SUMMARY OF U. S. FURNACE BLACK PLANTS
AND ATMOSPHERIC EMISSIONS FROM THESE FACILITIES
50-8

Plant Code Number	Unit Number	Date On-stream	Capacity, Tons Carbon Black/Yr.	Average Production, Tons/Yr.	Range in Production, % of Max.	Feedstock (f) (h)	Type of Carbon Black (f)	Emissions to Atmosphere
57,500	No seasonal variation Residuum tar	Drier Indirect Heat Source Vent	41,300	Drier Purge Vent	76,600	Storage Vent	Emergency Relief	(p)
		Process	211,800 (m)			4,800	28,400	
		Flow (a), Lbs./Hr.						
		Composition, (b) Tons/Ton Carbon Black						
		Particulate	0.0015					
		Carbon Dioxide	2.818	X				
		Carbon Monoxide	0.137					
		Hydrogen Sulfide	0.001					
		Sulfur Oxides (SO ₂ /SO ₃)	0.028					
		Hydrogen	0.010					
		Methane	0.002					
		Nitrogen & Argon	7.772					
		Oxygen						
		Nitrogen Oxides (NO ₂)						
		Water	6.087					
		Sample Tap Location						
		Date or Freq. of Sampling						
		Type of Analysis						
		HC, CO, CO ₂ & Inerts						
		Particulate						
		Hydrogen Sulfide						
		SO ₂ + SO ₃						
		NO _x						
		Odor						
		Vent Stacks						
		Number						
		Height						
		Diameter						
		Exit Gas Temp., °F						
		SCFM Per Stack (a)						
		Type of Recovery System						
		Electrostatic Precip.						
		Cyclone						
		Bag Filter/Total Compartments						
		Other						
		Date Installed						
		Vacuum Clean-up						
		Flow, SCFH (Air)						
		Particulate, T/H Carbon Black						
		Type of Recovery % Recov.						
		Stack Height/Diameter						
		Date Installed						
		Total Emissions, Ton/Ton Carbon Black						
		Hydrocarbons & H ₂ S (x)						
		Particulates						
		NO _x						
		SO _x						
		CO						

**SUMMARY OF U. S. FURNACE BLACK PLANTS
AND ATMOSPHERIC EMISSIONS FROM THESE FACILITIES**

Sheet - of 23

[illegible]

TABLE C3-3A. CONT.
SUMMARY OF U. S. FURNACE BLACK PLANTS
AND ATMOSPHERIC EMISSIONS FROM THESE FACILITIES

Plant Code Number

Unit Number

Date On-stream

Capacity, Tons Carbon Black/Yr.

Average Production, Tons/Yr.

Range in Production, % of Max.

Feedstock (F) (lb)

Type of Carbon Black (F)

Emissions to Atmosphere

Stream

Flow (a), Lbs./Yr.

Composition, (b) Tons/Ton Carbon Black

Particulate

Carbon Dioxide

Carbon Monoxide

Hydrogen Sulfide

Sulfur Oxides (SO₂/SO₃)

Hydrogen

Methane

Acetylene

Nitrogen & Argon

Oxygen

Nitrogen Oxides (NO₂)

Water

Sample Tap Location

Date or Freq. of Sampling

Type of Analysis

HC, CO, CO₂ & Inerts

Particulate

Hydrogen Sulfide

SO₂

NO_x

Odor

Vent Stacks

Number

Height

Diameter

Exit Gas Temp., °F

SCFH Per Stack (a)

Type of Recovery System

Electrostatic Precip.

Cyclone

Bag Filter/Total Compartments

Other

Date Installed

Vacuum Clean-up

Flow, SCFH (Air)

Particulate, T/T Carbon Black

Type of Recovery/% Recov.

Stack Height/Diameter

Date Installed

Total Emissions, Ton/Ton Carbon Black

Hydrocarbons & H₂S (x)

Particulates

NO_x

SO_x

CO

Process
116,700

Process
67,600

Transport Gas Vent
78,500

Transport Gas Vent
23,400

Storage Vent
27,800

Storage Vent
22,200

Combined
Drier Vent
96,800

No seasonal variation
Residuum tar
GPF

98,000

0.0006

0.0004

0.265

0.154

0.444

0.257

0.004

0.002

0.0002/0.0008

0.033

0.019

0.004

2.512

1.455

0.978

Same as 50-8

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2

82'

3'6"

375

13,800

60'

20.6"

375

9,580

70'

1'2"

70 - 150

2,850

3

82'

1'2"

150

1,700

2

75'

1'2"

150

2,550

5

36' - 40'

6"

130

1,210

4

49' - 52'

6"

130

1,210

14

58'

2'0"

650

1,740

11

1952 & 1970

1968

Yes

Filters - 1952 & 1953

4

16

4/32

0.006

0.002

0.0016

0.701

CB-16

TABLE CB-3A CONT.
SUMMARY OF U. S. FURNACE BLACK PLANTS
AND ATMOSPHERIC EMISSIONS FROM THESE FACILITIES

Plant Code Number		Sheet 10 of 23	
Unit Number		50-13	
Date On-stream		50-13	
Capacity, Tons Carbon Black/Yr.		2 & 3	
Average Production, Tons/Yr.		30,000 (e)	
Range in Production, % of Max.			
Feedstock (f) (h)			
Type of Carbon Black (f)			
Emissions to Atmosphere			
Stream			
Flow (a) Lbs./Hr.			
Composition, (b) Tons/Ton Carbon Black			
Particulate		Process 41,250	Drier 36,600 (s)
Carbon Dioxide		Process 69,200 (y)	Drier 18,300 (s)
Carbon Monoxide			
Hydrogen Sulfide			
Sulfur Oxides (SO ₂)			
Hydrogen			
Methane			
Acetylene			
Nitrogen + Argon			
Oxygen			
Nitrogen Oxides (NO ₂)			
Water			
Sample Tap Location			
Date or Freq. of Sampling			
Type of Analysis			
HC, CO, CO ₂ & Inerts			
Particulate			
Hydrogen Sulfide			
SO ₂			
NO _x			
Odor			
Vent Stacks			
Number		1	4
Height		160	172
Exit Gas Temp., °F		20,300	2,200 (s)
SCFM Per Stack (a)		X	X
Type of Recovery System		X	X
Electrostatic Precip.		X	X
Cyclone		X	X
Bag Filter/Total Compartments		X	X
Other		X	X
Date Installed			
Vacuum Clean-up			
Flow, SCFM (Air)			
Particulate, T/T Carbon Black			
Type of Recovery % Recov.			
Stack Height/Inchmeter			
Date Installed			
Total Emissions, Ton/Ton Carbon Black			
Hydrocarbons & H ₂ S (x)			
Particulates			
NO _x			
SO ₂			
CO			

TABLE CB-3A CONT.
SUMMARY OF U. S. FURNACE BLACK PLANTS
AND ATMOSPHERIC EMISSIONS FROM THESE FACILITIES

[illegible]

TABLE CB-24 CONT.
SUMMARY OF U. S. FURNACE BLACK PLANTS
AND ATMOSPHERIC EMISSIONS FROM THESE FACILITIES

Plant Code Number		50-23		Sheet 16 of 23	
Unit Number		1		2	
Date On-stream				3	
Capacity, Tons Carbon Black/Yr.				41,800 (e)	
Average Production, Tons/Yr.				34,500 (e)	
Range in Production, % of Max.				60 - 100	
Feedstock (f) (b)					
Type of Carbon Black (f)					
Emissions to Atmosphere					
Stream					
Flow (a), Lbs./Hr.					
Composition, (b) Tons/Ton Carbon Black					
Particulate					
Carbon Dioxide					
Carbon Monoxide					
Hydrogen Sulfide					
Sulfur Oxides (SO ₂)					
Hydrogen					
Methane					
Acetylene					
Nitrogen + Argon					
Oxygen					
Nitrogen Oxides (NO ₂)					
Water					
Sample Tap Location					
Date or Freq. of Sampling					
Type of Analysis					
HC, CO, CO ₂ & Inerts					
Particulate					
Hydrogen Sulfide					
SO ₂					
NO _x					
Odor					
Vent Stacks					
Number					
Height					
Diameter					
Exit Gas Temp., °F					
SCFM Per Stack (a)					
Type of Recovery System					
Electrostatic Precip.					
Cyclone					
Bag Filter/Total Compartments					
Other					
Date Installed					
Vacuum Clean-up					
Flow, SCFM (Air)					
Particulate, T/T Carbon Black					
Type of Recovery/Recov.					
Stack Height/Diameter					
Date Installed					
Total Emissions, Ton/Ton Carbon Black					
Hydrocarbons & H ₂ S (x)					
Particulates					
NO _x					
SO _x					
CO					
Process					
Drier					
Drier (s)					
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TABLE CR-3A CONT.
SUMMARY OF U. S. FURNACE BLACK PLANTS
AND ATMOSPHERIC EMISSIONS FROM THESE FACILITIES

Sheet 1 of 23

50-24

CR-25

Plant Code Number	1	2	3	4	5
Unit Number					
Date On-stream					
Capacity, Tons Carbon Black/Yr.			115,000 (e)		
Average Production, Tons/Yr.			109,000		
Range in Production, % of Max.			No Seasonal Variation		
Feedstock (f) (h)			Residual Fuel Oil		
Type of Carbon Black (f)					
Emissions to Atmosphere					
Stream					
Flow (a), Lbs./Hr.					
Composition, (b) Tons/Ton Carbon Black					
Particulate					
Carbon Dioxide					
Carbon Monoxide					
Hydrogen Sulfide					
Sulfur Oxides (SO ₂)					
Hydrogen					
Methane					
Acetylene					
Nitrogen					
Oxygen					
Nitrogen Oxides (NO ₂)					
Water					
Sample Tap Location					
Date or Freq. of Sampling					
Type of Analysis					
HC, CO, CO ₂ & Inerts					
Particulate					
Hydrogen Sulfide					
SO ₂					
NO _x					
Odor					
Vent Stacks					
Number					
Height					
Diameter					
Exit Gas Temp., °F					
SCFM Per Stack (a)					
Type of Recovery System					
Electrostatic Precip.					
Cyclone					
Bag Filter/Total Compartments					
Other					
Date Installed					
Vacuum Clean-up					
Flow, SCFM (Air)					
Particulate, T/T Carbon Black					
Type of Recovery/Recov.					
Stack Height/Diameter					
Date Installed					
Total Emissions, Ton/Ton Carbon Black					
Hydrocarbons & H ₂ S					
Particulates					
NO _x					
SO _x					
CO					

Process	153,600	Drier for Units 1 & 2	45,250	Process	153,600	Drier for Units 3, 4 & 4B	53,150	Process	51,550	Drier	9,800
	(1)		(1)		(1)		(1)		(1)		(1)

1970	None	Reasonably Accessible	None	1	1	1	1	1	1	1	1
G. C. (5A mole sieve & porepk Q)	None	All process vent streams	Slight H ₂ S Odor	108'0"	109'0"	102'0"	102'0"	102'0"	102'0"	102'0"	102'0"
None (Calc'd)	None			7'2"	3'10"	4'0"	4'0"	4'0"	4'0"	4'0"	4'0"
CdSO ₄ , weigh CdS (d)	46'0"			425	425	425	425	425	425	425	425
H ₂ O ₂ , form BaSO ₄ & weigh (d)	350			42,600	15,000	2,430	2,430	2,430	2,430	2,430	2,430
Phenol Disulfonic acid method	12,000			4,350	14,000	15,000	15,000	15,000	15,000	15,000	15,000
											</

Vacuum Clean-up

Flow, SCFM (Air)

Particulate, T/T Carbon Black

Type of Recovery/Recov.

Stack Height/Diameter

Date Installed

Total Emissions, Ton/Ton Carbon Black

Hydrocarbons & H₂S

Particulates

NO_x

SO_x

CO

Vacuum Clean-up

Flow, SCFM (Air)

Particulate, T/T Carbon Black

Type of Recovery/Recov.

Stack Height/Diameter

Date Installed

Total Emissions, Ton/Ton Carbon Black

Hydrocarbons & H₂S

Particulates

NO_x

SO_x

CO

TABLE CR-3A CONT.

Plant Code Number	Unit Number	Date On-stream	Capacity, Tons Carbon Black/Yr.	Average Production, Tons/Yr.	Range in Production, % of Max.	Feedstock (f) (h)	Type of Carbon Black (f)	Emissions to Atmosphere Stream	Process	Drier	Drier (g)
50-25 (K)	1	22,200	20,000	No consistent seasonal variation	Residual Fuel Oil	GPF	Residual Fuel Oil	Process 77,700	Drier 12,000	12,000	12,000
	2	19,400	17,500	Residual Fuel Oil	HAF		Residual Fuel Oil	Process 91,000	Drier 12,000	12,000	12,000
	4	17,800	16,000	Mixed Gas & Residual Fuel Oil	SRF		Mixed Gas & Residual Fuel Oil	Process 180,300	Drier 12,000	12,000	12,000
								0.0005	0.0005	0.0005	0.0005
								0.751	0.982	2.061	2.061
								1.173	1.330	2.922	2.922
								0.010	0.013	0.003	0.003
								0.027 (d)	0.031 (d)	0.025 (d)	0.025 (d)
								0.110	0.094	0.370	0.370
								0.037	0.025	0.126	0.126
								0.022	0.041	0.035	0.035
								7.670	10.334	23.930	23.930
								0.212	0.799	0.993	0.993
								0.0003	0.0024	0.0004	0.0004
								(c)	(c)	(c)	(c)
								1970	1970	1970	1970
								40 - 60 Ft. above ground. Accessible by stairs.			
								None	None	None	None
								G. C. (5A mole sieve & porepak Q)			
								None (Calc'd)			
								CdSO ₄ , weigh CDS (d)			
								H ₂ O ₂ , form NaSO ₄ & weigh (d)			
								Phenol Disulfonic acid method			
								No Complaints			
								8	2	2	16
								79'0"	79'0"	79'0"	78'6"
								2'6"	2'6"	2'6"	1'8"
								425	350	425	425
								2,800	3,200	3,460	3,460
								1/8	1/2	1	1
								Bag Filter/Total Compartments			
								1966	1971	1968	1968
								1/8	1/2	1/10	1/16
								1966	1971	1970	1968
								Spencer Vacuum System			
								which incorporates Bag Filter			
								on Drier Vent			
								1968			
								0.032	0.054	0.038	0.038
								0.0005 (t)	0.0005 (t)	0.0005	0.0005
								0.0003	0.0024	0.0004	0.0004
								0.0272	0.0312	0.0252	0.0252
								1,173	1,330	2,922	2,922

TABLE CB-3A CONT.

SUMMARY OF U. S. FURNACE BLACK PLANTS
AND ATMOSPHERIC EMISSIONS FROM THESE FACILITIES

Plant Code Number	Unit Number	Combined data for two units	50-26	50-27	50-28
Date On-stream	30,000	47,500 (n)	159,000 (Max. total for all units)	12,000	
Capacity, Tons Carbon Black/Yr.	24,000	No seasonal variation			
Average Production, Tons/Yr.		Cat. - Cracker Decant Oil			
Range in Production, % of Max.					
Feedstock (f) (h)					
Type of Carbon Black (f)					
Emissions to Atmosphere					
Stream	Drier Indirect	Drier	Process	Process	Storage and Product Handling
Flow (a), Lbs./Hr.	Source Vent	Purge Vent	162,800	44,000	Units. 1 & 2
Composition, (b) Tons/Ton Carbon Black	258,000	55,100	20,500	25,000	25,000
Particulate	X	X	.000024 (u)		
Carbon Dioxide			1.077	1.5 Ringelmann	
Carbon Monoxide			1.369	0.142	
Hydrogen Sulfide			TR		
Sulfur Oxides (SO ₂)	.008	.0013	TR		
Hydrogen			0.111		
Methane			0.021		
Acetylene			0.006		
Nitrogen + Argon	X	X	7.163		
Oxygen	X	X			
Nitrogen Oxides (NO ₂)	X	X			
Water					
Sample Tap Location					
Date or Freq. of Sampling					
Type of Analysis					
HC, CO, CO ₂ & Inerts					
Particulate					
Hydrogen Sulfide					
SO ₂					
NO _x					
Odor					
Vent Stacks					
Number	1	2	2	3	4
Height	135'0"	135'0"	73'0"	60'	57'0"
Diameter	7'6"	3'0"	1'6"	1'6"	1'5 1/2"
Exit Gas Temp. (a) (f)	960	800	350	400	200
SCFM Per Stack (a) (f)	70,800	6,000	2,750 (u)	3,750	2,850
Type of Recovery System					
Electrostatic Precip.					
Cyclone					
Bag Filter/Total Compartments	2/18	2			
Other	2 CO Boilers + Incinerator (1969)				
Date Installed		1969			
Vacuum Clean-up		Yes			
Flow, SCFM (Air)		500			
Particulate, T/T Carbon Black					
Type of Recovery % Recov.					
Stack Height/Diameter					
Date Installed					
Total Emissions, Ton/Ton Carbon Black					
Hydrocarbons & H ₂ S (x)					
Particulates					
NO _x					
SO _x					
CO					

TABLE CB-3A CONT.
SUMMARY OF U. S. FURNACE BLACK PLANTS
AND ATMOSPHERIC EMISSIONS FROM THESE FACILITIES
30-28 (Cont'd.)

Unit Number	3	3A	5	4	Storage & Product Handling for Units 3, 3A, 4 & 5
Date On-stream					
Capacity, Tons Carbon Black/Yr.	14,700	159,000 (Max. Total for all units)	12,200		
Average Production, Tons/Yr.	No seasonal variation	5,900			
Range in Production, % of Max.					
Feedstock (f) (h)	SO ₂ Extract Oil				
Type of Carbon Black (f)	Hard	Hard	Hard	Hard	
Emissions to Atmosphere					
Stream	Process	Process	Process	Process	Drier
Flow (a), Lbs./Hr.	161,200	66,600	138,400	40,200	32,100
Composition, (b) Tons/Ton Carbon Black					
Particulate	0.005	0.005	0.005	0.0012	0.0035
Carbon Dioxide	2.960	3.044	3.064	0.372	0.117
Carbon Monoxide	2.856	2.939	2.955	0.390	0.174
Hydrogen Sulfide	0.026	0.028	0.028	0.005	0.016
Sulfur Oxides (SO ₂)	0.014	0.014	0.014	0.003	0.008
Hydrogen	0.188	0.194	0.195	0.034	0.100
Methane	0.035	0.036	0.036	0.010	0.030
Acetylene	0.113	0.116	0.117	0.025	0.073
Nitrogen + Argon	21.387	22.009	22.067	2.974	8.924
Nitrogen Oxides (NO ₂)	0.0005	0.0005	0.0005	0.00	2.708
Water	20.449	21.044	21.199	0.0010	0.585
Sample Tap Location			Same as for units 1 & 2	0.0013	0.0013
Date or Freq. of Sampling				2.958	1.938
Type of Analysis					
HC, CO, CO ₂ & Inerts					
Particulate					
Hydrogen Sulfide					
SO ₂					
NO _x					
Odor					
Vent Stacks					
Number	1	6	12	4	3
Height	85'0"	71'6"	68'0"	59'6"	85'0"
Diameter	7'7"	1'5 1/2"	1'5 1/2"	1'5 1/2"	76'0"
Exit Gas Temp., °F	400	400	400	400	1'5 1/2"
SCFM Per Stack (a)	46,000	3,170	3,290	2,940	200
Type of Recovery System					80
Electrostatic Precip.					2,830
Cyclone					1,090
Bag Filter/Total Compartments	X	1/6	1/12	1/4	X
Other					3 Cylindrical & Venturi Water Scrubbers
Date Installed					
Vacuum Clean-up					
Flow, SCFM (Air)					
Particulate, 1/1 Carbon Black					
Type of Recovery/Recov.					
Stack Height/Diameter					
Date Installed					
Total Emissions, Ton/Ton Carbon Black					
Hydrocarbons & H ₂ S					
Particulates					
NO _x					
SO _x					
CO					

CB-28

TABLE CB-3A CONT.
SUMMARY OF U. S. FURNACE BLACK PLANTS
AND ATMOSPHERIC EMISSIONS FROM THESE FACILITIES

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50-30

Plant Code Number

Unit Number
Date On-stream

Capacity, Tons Carbon Black/Yr.
Average Production, Tons/Yr.

Range in Production, % of Max.
Feedstock (f) (h)

Type of Carbon Black (f)
Emissions to Atmosphere

Stream

Flow (a), Los./Hr.

Composition, (b) Tons/Ton Carbon Black

Particulate

Carbon Dioxide

Carbon Monoxide

Hydrogen Sulfide

Sulfur Oxides (SO₂)

Hydrogen

Methane

Acetylene

Nitrogen+ Argon

Oxygen

Water

Nitrogen Oxides (NO₂)

Sample Tap Location

Date or Freq. of Sampling

Type of Analysis

HC, CO, CO₂ & Inerts

Particulate

Hydrogen Sulfide

SO₂

NO_x

Odor

Vent Stacks

Number

Height

Diameter

Exit Gas Temp., Of

SCFM Per Stack (a)

Type of Recovery System

Electrostatic Precip.

Cyclone

Bag Filter/Total Compartments

Other

Date Installed

Vacuum Clean-up

Flow, SCFM (Air)

Particulate, T/T Carbon Black

Type of Recovery/ Recov.

Stack Height/Diameter

Date Installed

Total Emissions, Ton/Ton Carbon Black

Hydrocarbons & H₂S (x)

Particulates

NO_x

SO_x

CO

60,000 (m)

No seasonal variation
Oil (1.5 PSI V. P. @ 120° F)

+0.000 (m)

No seasonal variation
Oil (1.5 PSI V. P. @ 120° F)

Primary Process	Pneumatic Conveyor	Drier	Primary Process	Pneumatic Conveyor	Drier	Primary Process	Pneumatic Conveyor	Drier
316,200	21,300	44,600	190,500	16,800	35,250	190,500	16,800	35,250
0.0001	0.00006	Nil	0.0001	0.00007	Nil	0.0001	0.00007	Nil
0.857			0.750			0.750		
1.600			1.625			1.625		
0.020			0.010			0.010		
0.007			0.003			0.003		
0.059			0.100			0.100		
0.021			0.025			0.025		
0.057			0.032			0.032		
11.494	1.437 (j)	2.057 (j)	9.583	1.667	2.375 (j)	9.583	1.667	2.375 (j)
(c)		1.000	(c)		1.250	(c)		1.250
	None (calc'd)			None (calc'd)			None (calc'd)	
Slight SO ₂ & H ₂ S			Slight SO ₂ & H ₂ S			Slight SO ₂ & H ₂ S		
3	2	1	3	3	1	3	3	1
83'	101'	116'	101'	101'	90'	101'	101'	90'
4'5"	1'3"	1'6"	4'6"	1'3"	3'1"	4'6"	1'3"	3'1"
400	Atmos.	300	400	Atmos.	300	400	Atmos.	300
28,950	2,275	11,700	18,000	1,220	9,600	18,000	1,220	9,600
X	X	X	X	X	X	X	X	X
1961	1969	1961	1969	1969	1969	1969	1969	1969
	0.077			0.042			0.042	
	0.0002			0.0002			0.0002	
	0.007			0.003			0.003	
	1.600			1.625			1.625	

TABLE CB-3A FOOTNOTES

Sheet 22 of 23

a) Wet gas flow rate based on carbon black average production rate unless otherwise noted. If average production figures not shown, flow rate is based on maximum plant capacity.

b) Average composition, actual values depend on type and quantity of carbon black being produced.

c) Stream contains 45 + 2 vol. % water.

d) Reference "Atmospheric Emissions from Sulfuric Acid Manufacturing Processes" U. S. Dept. of Health, Education and Welfare. Subsequent analysis has not confirmed the presence of SO₂.

e) Total for all units at this location.

f) Particular type corresponding to emission composition shown, actual feedstock and type of carbon black can vary.

g) Processed in unit No. 1 facility. Separate drier filter to be installed in September, 1972.

h) In all oil furnace plants 15-25 wt. % of feed consists of natural gas or other light hydrocarbons. In mixed feed units, percentage of feed gas is higher.

j) Air.

k) Also have pilot plant which is not shown in this summary.

l) Approximate emissions from the various process vent stacks can be obtained by prorating emissions shown for other units operated by same company. Prorating factor is directly proportional to total vent gas flow rate and inversely proportional to carbon black production rate.

m) Volume flow before combustion of gases. Composition shown is estimate of flare effluent assuming 20% of particulate carbon black and 90% of other combustibles are burned. Composition excludes excess oxygen and nitrogen resulting from combustion air.

n) Total for all three units in this facility.

o) Includes drier vent from No. 4 unit.

p) Maximum flow all relief stacks venting at same time. Normally no flow. During individual furnace warm-up, flow is vented to atmosphere. At this time, maximum flow is equal to volume shown for one stack. During initial part of warm-up, vent will contain no carbon black.

q) Isokinetic gas sampling used for particulate.

r) Total process vent emissions from all units located at this plant. Composition of vent stream is based on intermediate values of component composition ranges provided by this company for producing various types of carbon black in their plants.

s) Assumed value based on generalized data provided in survey.

TABLE CB-3A FOOTNOTES (CONTINUED)

t) Total losses, including spills and leaks, estimated to be 0.001 tons per ton of carbon black product.

u) Value estimated by carbon black manufacturer.

v) Calculated based on emission factor of 0.23 lb. NO₂/1000 cu. ft. of gas burned while reactors are on inert operation.

w) ASTM-N500 series.

x) Excludes hydrogen and methane.

y) Same as footnote (1) except prorated emissions shown for plant 50-11.

z) Same as footnote (1) except prorated emissions shown for plant 50-19.

TABLE CB-4
TYPICAL VENT GAS COMPOSITION
FOR
90 MM LB./YR. CARBON BLACK PRODUCTION
FROM FURNACE OIL PROCESS

<u>Component</u>	<u>Range in Composition</u>	<u>"Typical" Flow Rate</u>		
	<u>Mol % (a)</u>	<u>Mol/Hr.</u>	<u>Lbs./Hr.</u>	<u>Mol %</u>
Hydrogen	5.5 - 15	609.6	1,229	6.7
Carbon Dioxide	3 - 6.5	226.8	9,978	2.5
Carbon Monoxide	6 - 14	502.5	14,071	5.5
Hydrogen Sulfide	0.01 - 0.2	9.0	306	0.1
Sulfur Oxides				
SO ₂	TR - 0.03 (d)	TR	TR	TR
SO ₃	TR	-	-	-
Methane	0.2 - 0.7	19.8	318	0.2
Acetylene	0.1 - 1.0	14.8	383	0.2
Nitrogen & Argon	65 - 80	3,222.1	90,686	35.5
Oxygen	0 - 4.9 (c)	25.3	810	0.3
Nitrogen Oxides (NO ₂)	15 - 200 ppm (d)	0.4	18	44 ppm
Carbon Black			24 (b)	
Water	(a)	<u>4,456.8</u>	<u>80,223</u>	<u>490</u>
		9,087.1	198,046	100.0

(a) Dry basis, stream contains 42-50 mol percent water. Reported ranges include all questionnaires.

(b) Reactor effluent stream to product recovery contains 11,035 lbs./hr. carbon black.

(c) Presence of oxygen only reported by several carbon black manufacturers. This oxygen may be a result of air leakage into the effluent stream or test sample prior to analysis.

(d) High values represent data from two plants. However, most producers believe actual value is toward low end of range shown.

parallel trains of equipment with multiple reactors. These reactors and other equipment can be put in and out of service as production demands vary. Since product recovery bag filters and other emission control devices remain in service during start up and shut down operations, emissions do not increase under these circumstances.

In addition, because of multiplicity of equipment, individual processing upsets usually will not result in significant variations in atmospheric emissions. However, this is not always true in regard to problems that can occur with product recovery equipment. Particulate emissions from the process vent stream can greatly increase if substantial leaks develop in the product bag filters.

2. Product Transport

If the carbon black plant incorporates pneumatic conveyors for moving product to the finishing area, the carrier gas may be vented after recovery of entrained carbon black. Some plants use a closed loop system and eliminate this venting.

3. Drier Vent

(a) Indirect Heat Source

In most plants a large portion of the hot gas employed in the drying operation does not come in direct contact with the carbon black but is used as an indirect heat source and, therefore, contains no entrained carbon black.

(b) Purge Gas

Anywhere from 35 to 70 percent of the gas is directly charged to the drier interior for removal of water vapor. This purge gas picks up carbon particles and is usually vented after passing through a filter or water scrubber for particulate removal.

4. Bagging and Storage Area Vent

Carbon black content of this air stream varies depending upon specific operations being performed in the storage area. However, since storage and bagging areas are usually within a building, a vacuum clean-up system which rejects filtered air is typically included.

B. Intermittent Air Emissions

1. Vacuum Clean-up

The vacuum system is normally in continuous operation. However, carbon black is only present in the exhaust air when the facilities are being used to clean-up carbon spills. In some plants bagging and storage areas are tied into the vacuum system in which case carbon black emissions would be on more of a continuous basis.

2. Emergency Relief

In some plants the furnace reactors are directly vented to the atmosphere during reactor warm-up. This venting is very infrequent and only occurs when a new reactor is put in service to meet increased production requirements. Reactor warm-up is accomplished by burning

natural gas and the reactor is put on line before adding oil feed. Therefore, no carbon black or hydrocarbons are emitted during the direct venting operation.

C. Liquid Wastes

Liquid wastes are usually not discharged from these units. Normally, any effluent water recovered from vent gas scrubbing operations is used as supplemental reactor effluent quench in order to reduce the net process water requirement and recover entrained carbon black. Water is used in many plants to clean-up carbon black spills. This water is normally collected in a pond where it is either allowed to completely evaporate or is used as supplemental make-up water for reactor effluent quench system.

D. Solid Wastes

Solid wastes consist of used filter bags (0.3 to 0.5 lbs./ton of carbon black) and used furnace refractory bricks (0.7 to 1.5 lbs./ton of carbon black) which are discarded as land fill. In addition, pond sludge, which varies in quantity between 0 to 40 lbs./ton of product, is also normally used as land fill.

IV. Emission Control Devices and Systems

A. Early Methods of Product Recovery

Prior to about 1965, most units recovered product from the quenched furnace effluent by means of electrostatic precipitators and several stages of cyclone collectors (usually three) with or without wet gas scrubbers. With this type of recovery system, it was possible to recover up to about 92 percent of the contained carbon black. Based on present high sales volume of ultra-fine products, estimated collection efficiency for this type of recovery system would drop to 87 or 88 percent. The remaining carbon black would be vented to the atmosphere with the combustion gases. During this earlier time period, most drier vents were exhausted directly to atmosphere.

B. Bag Filters on Process and Drier Vents

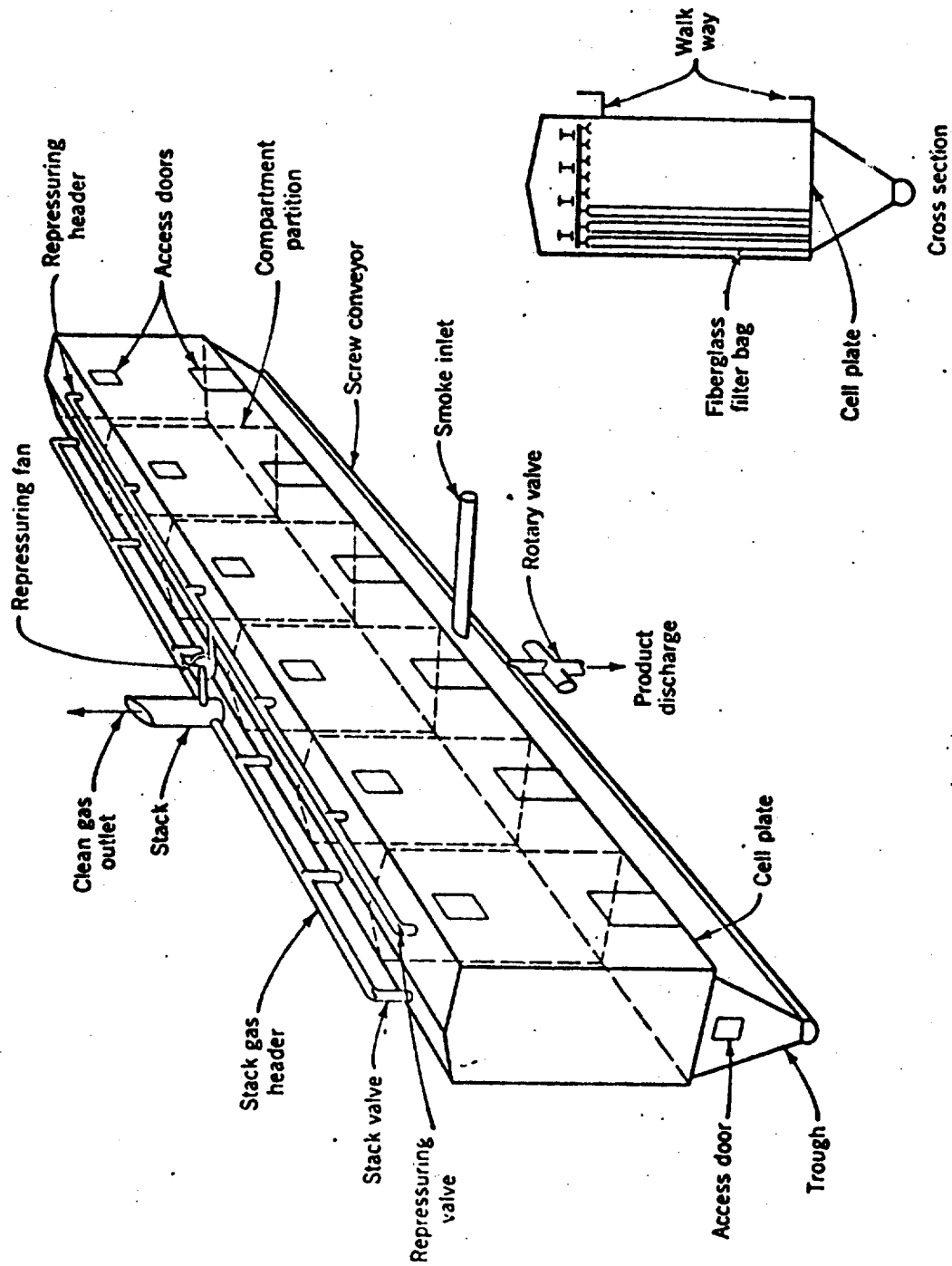
In order to improve product yield and reduce emissions, nearly all present furnace type carbon black plants incorporate bag filters in the product recovery system. The bag filter has either been added on, or replaced the precipitator and/or the cyclones in existing plants. In addition, bag filters on the furnace effluent and drier vent streams are reported to obtain up to 99.95 percent carbon black recovery.

The substantial improvement in product recovery obtained by utilizing bag filters on the main process vent stream economically justifies the increased investment, utilities and maintenance cost for this equipment. However, this is not usually true in regard to filters placed on drier vent streams and filters used in the product finishing plus storage areas in order to minimize carbon black emissions. Without this particular equipment, approximately 1.5 percent of the carbon black production would be lost. Recovery of this relatively small amount of material does not economically justify the relatively high bag filter investment and operating costs involved.

A sketch of a typical bag filter design for the main process vent stream is shown in Figure CB-2. Carbon black-laden gases enter the hopper below the bag cell plates. The hopper performs as a distribution duct for the entering production stream. The process gases and carbon black flow into the individual bags of each compartment through cell plates. The filtered gas flows through the bags and out the bag filter stacks. The entrained carbon black collects on the inside of these bags, and during the cleaning or repressure cycle of each compartment, the black is removed and dumped into the hopper (repressuring simply means that the flow of gas through the bags is reverse, Figure CB-3). From the hoppers, the carbon black is usually either dropped through air locks into a pneumatic conveyor system or fed to screw conveyors for transportation to the product finishing area.

Figure CB-2 shows a single stack for the entire bag filter. In some cases, the filters have one stack for each compartment. This makes it somewhat easier to locate leaking bags.

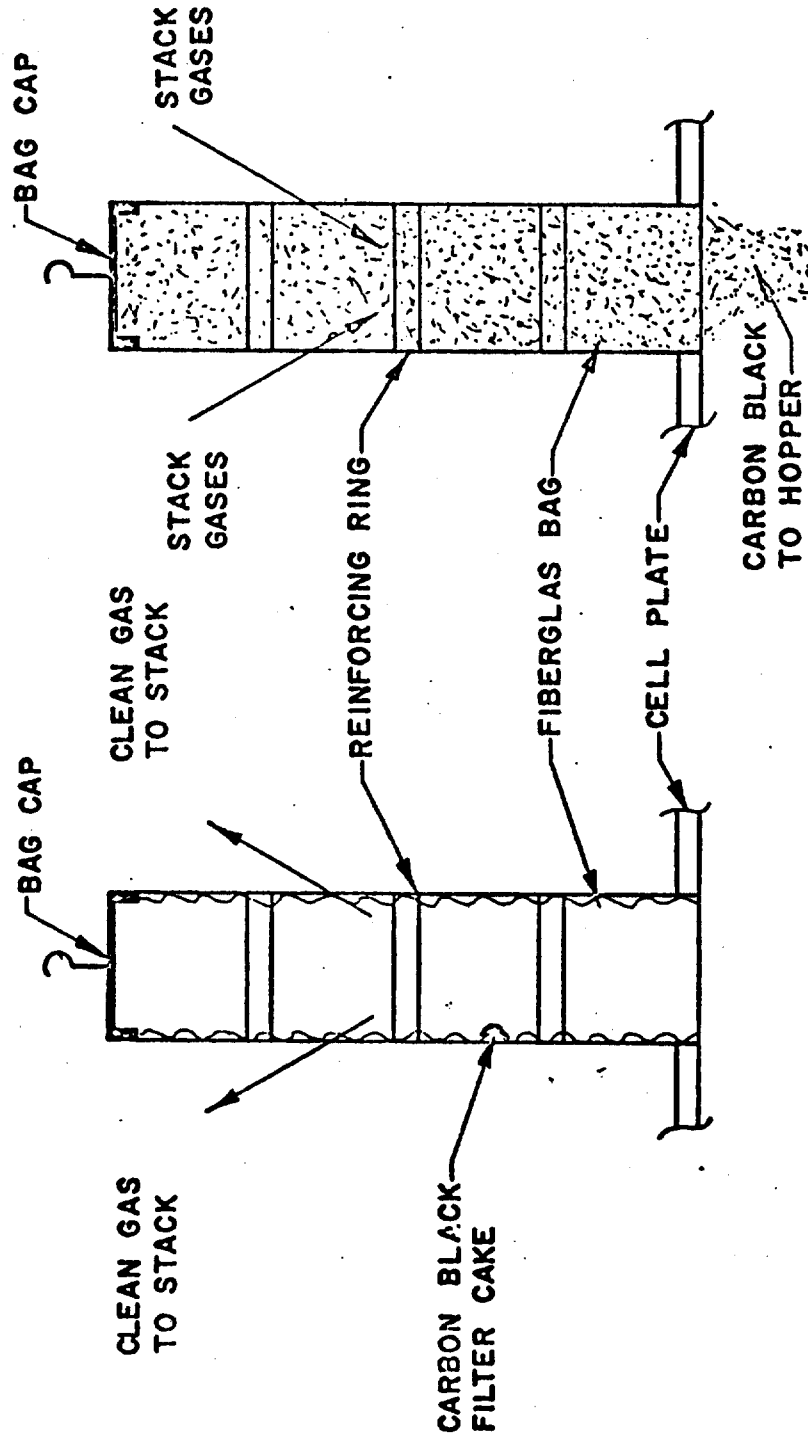
Normally, the main process vent bag filters contain 6 to 18 compartments and each compartment contains approximately 300 to 400 bags. Each bag is about 5½ inches in diameter and 126 inches (10½ ft.) long. These bags themselves are a great cost item in the bag filter. Bag filter material



Carbon black filter.

FIGURE CB-2

FIGURE CB-3
FILTER BAG CLEANING PROCESS



FILTERING CYCLE CLEANING CYCLE

used by most major black producers consists of fiberglass which is coated with a graphite-silicon film. Bag life would be seriously reduced if this coating were removed, and this can easily happen if operating temperature is allowed to exceed 450° F.

The average life expectancy of the filter bags is about 12 to 18 months. However, it is usually necessary to replace a few bags in each compartment during this period. High sulfur content of the oil or impurities in the quench water can shorten this life.

The bags are normally supported from hangers in the roof of the filter compartment with metal caps. The caps are tapered on the sides and are slightly larger in diameter than the hem around the top of the bag. The caps are inserted into the bags edgewise. When the cap is rotated and pulled outward, the bag is wedged around the perimeter of the cap. The wedging action seals the cap-bag surface and provides support for the bags. The bottom of each bag is then secured with a snap ring onto the cell plate.

The repressuring process is controlled with an electrically operated timer.² Figure CB-4 illustrates the principal operations of the bag filter. As shown, the first two compartments are filtering carbon black from process gases as the No. 3 compartment is being cleaned. The next event in the operation will be cleaning of compartment No. 1 while filtration continues in the No. 2 and No. 3 compartments. This step-like rotation is continued until all compartments have been repressured. The cycle is then repeated.

The repressuring fan generates enough force to reverse the flow of gases. The gases used in the cleaning cycle are taken from compartments on the filtering cycle. In Figure CB-4, compartments No. 1 and No. 2 are supplying the repressuring gases for compartment No. 3. When compartment No. 1 is cleaned, the gases will be provided from compartment No. 2. The three compartment filter illustrated is merely schematic. On commercial bag filters, several of the compartments are used as a source for repressuring gas.

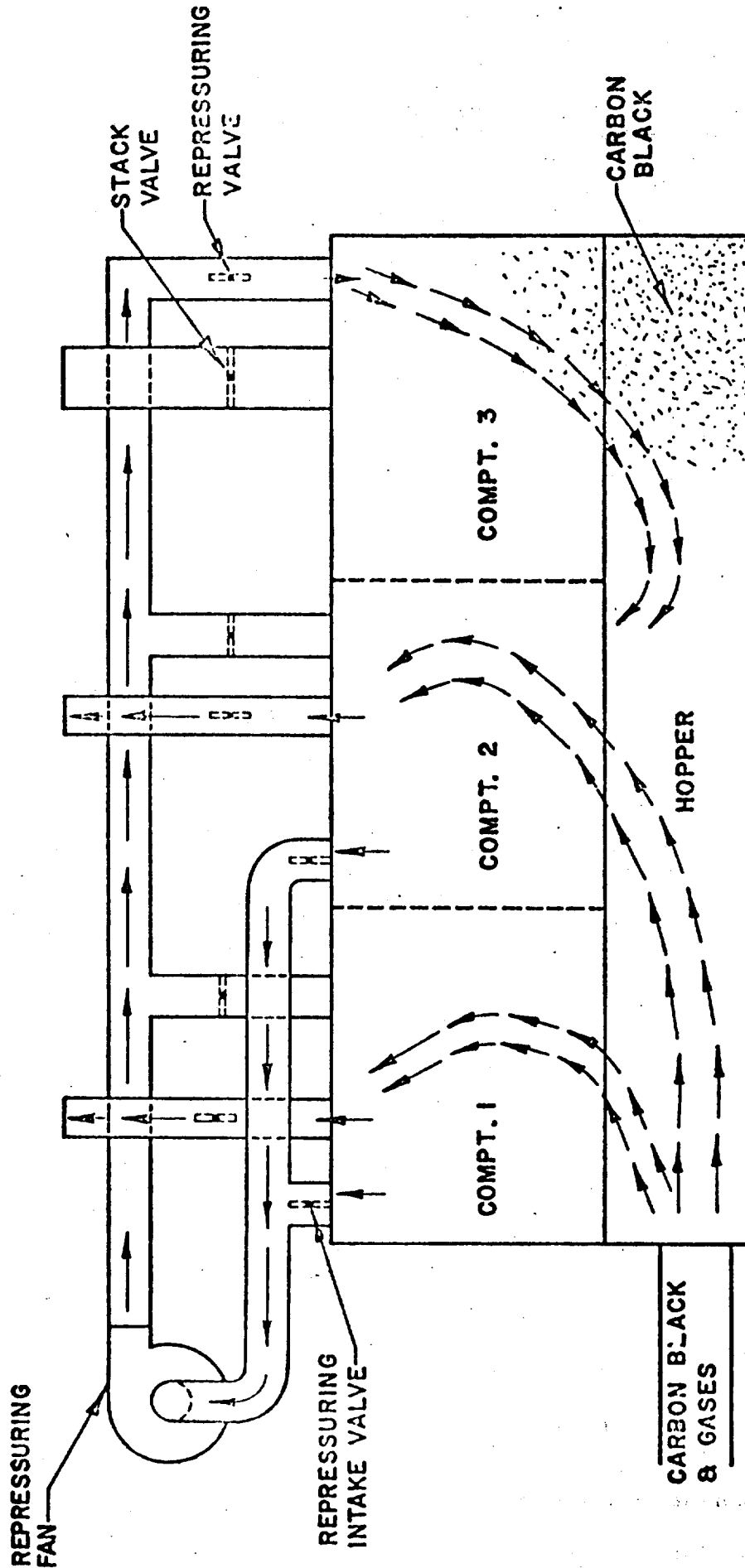
The sequence of events which puts compartment No. 3 on-and-off the cleaning cycle is:

1. Stack valve closes.
2. Repressuring valve opens.
3. Cleaning cycle.
4. Repressuring valve closes.
5. Stack valve opens.
6. Filter cycle.

For cleaning compartment No. 1, the sequence is slightly different because of the repressuring intake valve. When the stack valve closes, so does the repressuring intake valve; and when the stack valve opens, the repressuring intake valve opens.

Similar type bag filters are used to recover carbon black from the

FIGURE CB-4
BAG FILTER OPERATION*



*typically 8-12 compartments only 1 out for cleaning

drier purge vent gas. Fiber glass bags are used in these filters because of the normal 400° F and higher operating temperatures.

Corrosion, and its related maintenance cost, is a continuous problem in bag filters, especially in drier vent applications. This is due to both the sulfur and the water content of the exit gases.

C. Water Scrubbers for Particulate Removal

Water scrubbers are somewhat less efficient (90 to 95%) than bag filters and are being phased out of product recovery service. They are still used in drier purge gas clean-up service because of their lower costs. In some plants, carbon black losses in drying and product finishing areas are more than 1.5%. Under these circumstances, water scrubbing of the drier vent gas and other product finishing vent streams for carbon black recovery can be economically justified. However, the product trend in carbon black specifications is toward materials that are harder to wet, thus decreasing the effectiveness of scrubbers.

One carbon black producer (50-28) incorporates the following relatively efficient water scrubbing system on the drier vent stream. A blower located downstream of a tangential entry vertical cylindrical scrubber pulls vent gas from the drier. Discharge gas from the blower is sent to a Venturi scrubber. Essentially, this is three stages of scrubbing since water is sprayed into the cylindrical scrubber, blower inlet and Venturi scrubber. The Venturi scrubber discharges into a cyclone separator and out through a stack to the atmosphere. Slurry is collected from the cylindrical scrubber and from the cyclone separator. Some of the slurry is recycled to the scrubber sprays and the remainder is used for quenching reactor effluent gas. In this way, all of the black removed from the drier vent gas stream re-enters the normal production train.

Total water usage for the scrubber system is about eight gallons per 1000 SCF of gas processed. Of this total about 33 percent is fresh water and 67 percent is recycled slurry. Total pressure drop through the system is about 15" H₂O.

D. Pneumatic Conveyor Exhaust Gas Clean-up

In plants where air pneumatic conveyors are used to transport carbon black to the product finishing area, the transport medium is usually sent to a bag filter for carbon black recovery before this gas is vented to the atmosphere. Because of the low temperatures involved, wool, cotton or orlon bags are used in these "secondary" bag filters.

E. Clean-up System for Miscellaneous Particulate Emissions

In addition to the above carbon black losses, particulate emission can occur from the following sources:

1. Inadvertent spillages when drawing samples from production line.
2. Unplugging production line stoppages.
3. During cleaning of process equipment and hopper cars.
4. Leaks that develop in process equipment.
5. Bagging operation and loading of hopper cars.

6. Bags torn during stacking in warehouse or loading and unloading of box cars or trucks.

Most plants minimize these emissions by improved operating methods, preventive maintenance and employment of a vacuum clean-up system as shown in Figure CB-5. By having multiple hose connections on a vacuum line throughout the plant, it is possible to pick up and recover most carbon black spills. In addition, vacuum packing of bags in a hermetically sealed product packing system will prevent carbon black emissions from this source.

Installed cost for a vacuum system similar to that shown in Figure CB-5 for an average size carbon black plant would be \$20,000 to \$50,000.

Typical average overall carbon black recovery for a plant containing bag filters on vent streams and a vacuum system for clean-up is about 99.9%.

F. Combustion Devices for Process Vent Gas

In addition to the above equipment which reduces particulate emissions, some carbon black plants have pollution control devices on process vent gas streams to reduce CO and H₂S emissions to the atmosphere. These devices include CO boilers, incinerators and off-gas plume burners. It is also conceivable that catalytic oxidation could be employed. Use of this various equipment will tend to increase carbon black manufacturing cost.

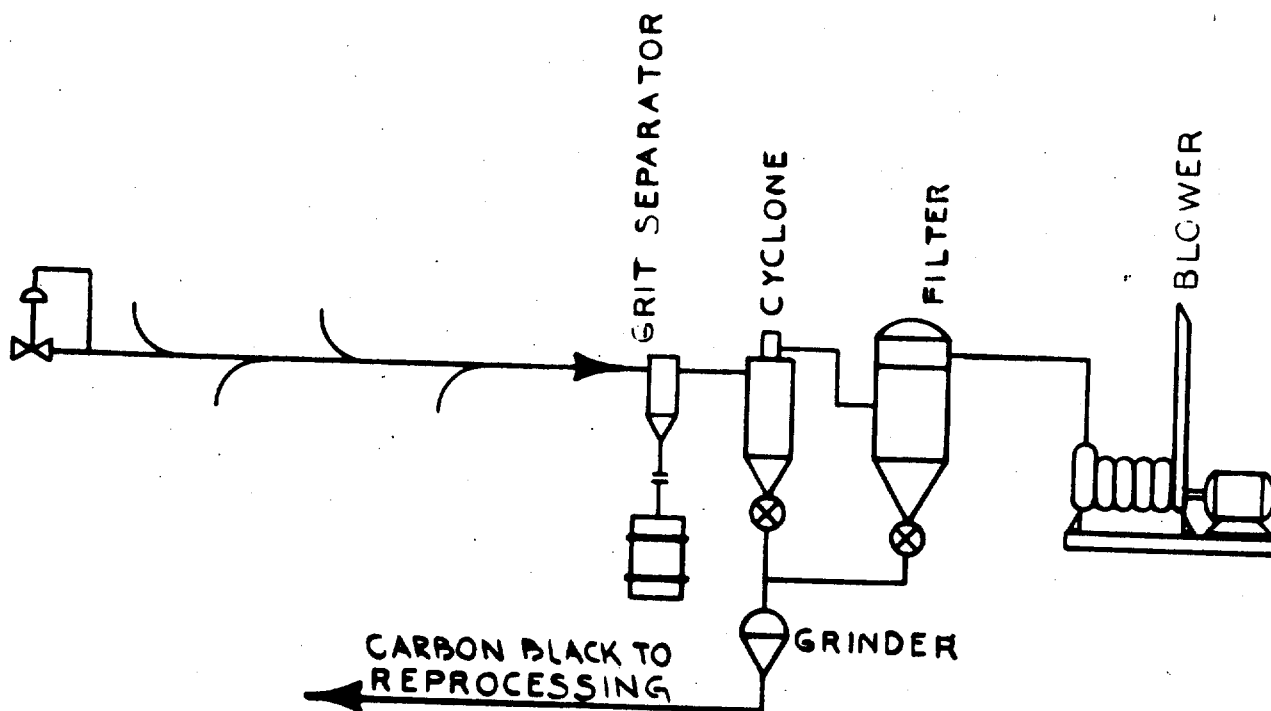
1. Devices in Use in the U.S.A.

a. CO Boilers

Table CB-5 illustrates a CO boiler and provides the material balance that would be expected if controlling the "typical" emission as tabulated in Table CB-4. It should be noted that this type of installation requires supplemental fuel and requires no heat exchange systems other than those to preheat and vaporize the boiler feed water and superheat the steam. It will typically produce more steam than can be economically used in a carbon black plant, so a choice must be made between exporting some of the steam or burning some of the CO in a different manner.

The addition of a CO boiler is one of the more efficient methods of controlling combustible gaseous emissions. However, by-product steam credits can not usually off-set operating costs. It is doubtful if the addition of a CO boiler to any existing carbon black plant is practical since most of these units have motor driven equipment and could not use generated steam without a large expenditure for turbine drivers. Vent gas effluent from the CO boiler will contain no particulates, CO and H₂S. In order to insure complete combustion of these components, it is normal practice to design for a 1600 to 1800° F operating temperature in the boiler combustion zone. In addition, excess air is employed (2 to 4 mol % O₂ in boiler effluent - dry basis). The data in Table CB-5 are based on an 1800° F combustion zone temperature and 4 mol % oxygen (dry basis) in the stack gas.

Only one existing U.S. plant utilizes CO boilers. This plant (50-26) represents the best emission controlled U.S. carbon black



FOR
ENVIRONMENTAL PROTECTION AGENCY
CONTRACT NO. 68-02-0255

DR BY	J. L.	7-5-72
CH BY	WAS	10-18-72
APPD	Jm	11-7-72
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DATE FINISHED		

CATALYTIC, INC.
ENGINEERING DEPT., PHILA., PENNA 19102

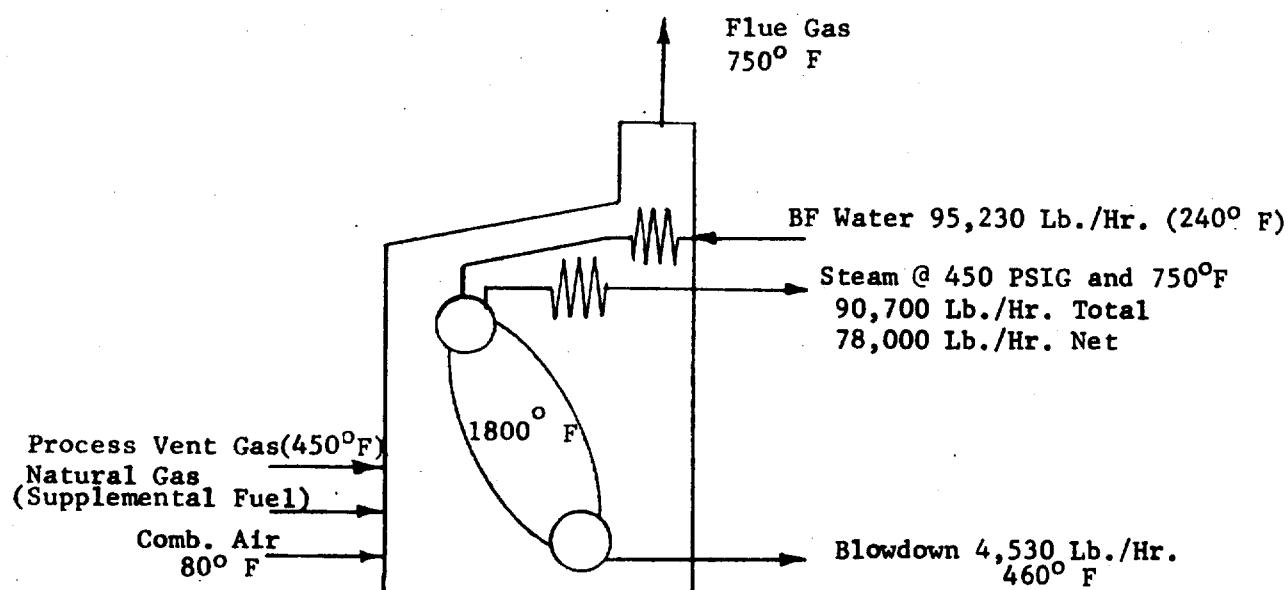
FIGURE CB-5
TYPICAL VACUUM
CLEANUP SYSTEM

DATE	RECORD OF ALTERATIONS	BY	APPD	APPD	SCALE	PROJECT NO.	I.D. NO.	DRAWING NO.	REV. NO.
					—	42030	509	R-241	A

TABLE CB-5
CO-BOILER EMISSION CONTROL SYSTEM
FOR
90 MM LB./YR. FURNACE BLACK PLANT

OVERALL MATERIAL BALANCE, LB./HR.

<u>Component</u>	<u>Process Vent Gas</u>	<u>Comb. Air</u>	<u>Natural Gas</u>	<u>Flue Gas</u>
H ₂	1,229			
CO ₂	9,978			36,604
CO	14,071			
H ₂ S	306			
S+SO ₂	TR			578
CH ₄	318		677	
C ₂ H ₂	383			
C ₂ H ₆			149	
Carbon Black	24			
N ₂	90,686	111,588	70	202,334
O ₂	810	33,804		10,753
H ₂ O	80,223	1,580		95,603
NO _x	18			42
TOTAL LBS./HR.	198,046	146,972	896	345,914
SCFM	57,400			85,000



plant. Boilers were incorporated in the original plant design and the decision to burn off-gases was primarily for purposes of odor control since this plant is located in a metropolitan area. The choice of a CO boiler rather than an incinerator was based on energy costs. Because of operating and maintenance difficulties, this particular carbon black manufacturer feels that a complete new study would be undertaken before they would again choose a CO boiler for a new plant. The present plant went on stream about 1970.

Problems with off-gas burning in CO boilers include the following:

- i Vent gas is available at low pressure.
- ii Gas stream is corrosive.
- iii Investment for required blowers, large diameter pipes and valves, burning equipment, control systems and steam utilization systems is high. This is especially true if a spare boiler is provided for dependable steam supply.
- iv Because of the low heating value (30 to 50 BUT/FT.³) of the gas stream, up to 35% of the total heating value must be added as supplemental fuel in order to achieve complete combustion.
- v Flame control is difficult due to low heating value and low level of incandescence, therefore, flameouts and their inherent safety hazards are common.
- vi An operating problem results from the need to switch to complete fuel gas firing whenever a different type of black is to be produced. This is necessary because oil is cut out and complete system is purged of black before change over can be made. Coming back on the line is then difficult. Such changes are frequent.

In the 50-26 facility, as would most likely be true in most carbon black plants generating steam, not all the process vent gas is sent to the CO boilers. Steam would have to be exported if total available heat was used to generate steam. At the 50-26 plant electric stand-bys are provided on several key pumps, otherwise all main equipment is steam driven except start-up units. On this basis about 60% of the process vent gas is charged to the boilers, 10% is used in the carbon black driers and the remainder is sent to an incinerator.

The thermal incinerator employed at plant 50-26 is not a recommended type since it employs supplemental fuel but does not recover heat from either the process vent gas or the fuel. Hence, the anticipated material balance would be as shown on Figure CB-5 but with only about 47,000 lbs./hr. of net steam produced. The economics of this scheme are poor and its environmental impact is unfavorable. Therefore, it is not considered in this report.

b. Plume Burners

Off-gas plume burners are known to be used by only one existing carbon black manufacturer (plants 50-7 and 50-8), but it has been reported that retro-fit burners without supplemental fuel have been

successful, both domestically and in Europe. This control device has the following limitations:

- i Efficiency for removal of contaminants is relatively poor. Degree of combustion obtained depends on BTU content of the vent gas. If a high yield carbon black is being produced, a rich vent gas will result and it is estimated that 95% or more of the CO, H₂S and hydrocarbons will be burned. For other type carbon black production, heating value of the vent gas will be lower and only about 75-80% of these impurities will be oxidized. It is estimated that 20-30% of the vented carbon black is burned.
- ii Small changes in vent gas composition could extinguish the burner if supplemental fuel and adequate instrumentation are not provided.
- iii Improper firing of the burner could result in operating temperatures which favor NO_x formation.

The industry nomenclature distinguishes between plume burners and flare stacks as devices which, respectively, do not or do require supplemental fuel. According to the operator of the plants which have plume burners, the minimum self supporting heating value is about 50 BTU/scf with their normal operation between 70 and 100 BTU/scf. The "typical" vent gas of this study has a heating value of about 40 BTU/scf and thus is not adaptable to plume burning. If flared, supplemental fuel will be required and the consensus is that sufficient fuel to raise the heating value to 100 BTU/scf is the minimum for a stable flame. The consensus also is that flaring of the 100 BTU/scf gas will achieve only "about 90% combustion". No one is willing to predict the nature of the other 10% but it is safe to assume that is a mixture of unburned CO and hydrocarbons and "cracked" products such as ethylene and soot. The proportions of these are variable and unknown, hence a material balance for the control system is not included in this report.

2. Devices Not Currently in Use in the U.S.A.

a. Thermal Incinerator

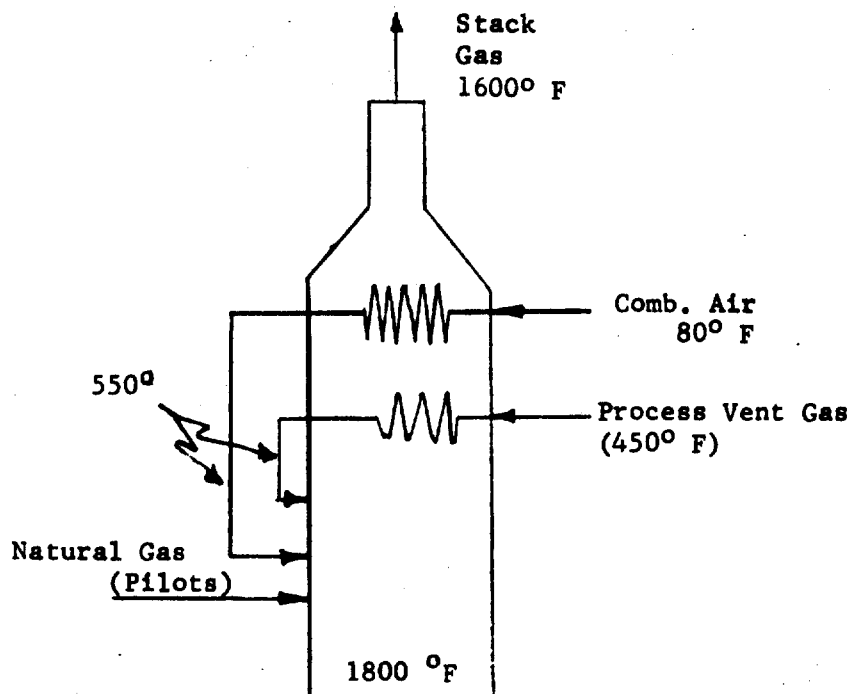
Table CB-6 presents a material balance for a thermal incinerator that includes a section of air and vent gas preheat by heat exchange against the products of combustion. It is based on 1800° F combustion zone temperature and 4 mol % oxygen in the stack gas. This technique, as illustrated on the table, results in essentially complete combustion without any supplemental fuel (except pilots) and thus is a recommended technique if no need exists for steam generation since it results in the waste of a minimum amount of energy.

Burning of off-gas in a thermal incinerator of this type results in off-gas burning problems and combustion efficiency similar to that obtained with a CO boiler. Heat recovery from the burning of the process vent gas is sufficient to obtain the desired operating temperature. This is based on vent gas having a heating value of 40 BTU/FT.³. If heating value of the gas differs appreciably from the typical value given in Table CB-4, heat balanced operation can

TABLE CB-6
THERMAL INCINERATOR
FOR
90 MM LB./YR. FURNACE BLACK PLANT

OVERALL MATERIAL BALANCE, LB./HR.

<u>Component</u>	<u>Process Vent Gas</u>	<u>Air To Incin.</u>	<u>Stack Gas</u>
H ₂	1,229		
CO ₂	9,978		34,308
CO	14,071		
H ₂ S	306		
S+SO ₂	TR		578
CH ₄	318		
C ₂ H ₂	383		
NO _x	18		34
Carbon Black	24		
N ₂	90,686	98,553	189,230
O ₂	810	29,848	10,060
H ₂ O	80,223	1,396	93,633
TOTAL LBS./HR.	198,046	129,797	327,843
SCFM	57,400		82,500



be obtained by adjusting the amount of preheat. This system is not presently used in the U.S. and sulfur corrosion and metalurgy problems might occur in the preheat section.

At present only the previously mentioned 50-26 carbon black plant is known to incorporate a thermal incinerator in the U.S.A. At this plant more excess air is used than is normally proposed (7 vs. 4 mol % O_2) and there is no air preheat. For these reasons, supplemental fuel is required.

b. Incineration Plus Steam Generation by CO-Boiler

Table CB-7 presents a material balance and sketch of a combination CO-boiler and thermal incinerator system for a 90 MM lbs./yr. furnace black plant. Steam production is limited to estimated on-site requirements (60% of process vent gas to CO-boiler). This depicts essentially the practice followed at plant 50-26 but incorporates the more economical thermal incinerator described above so as to minimize supplemental fuel requirements. It requires two units, one utilizing a preheat section for burning excess vent gas without additional fuel and the other a CO-boiler that provides the process steam requirements without heat exchange but with fuel to support combustion.

c. Incineration plus Steam Generation by Waste Heat Boiler

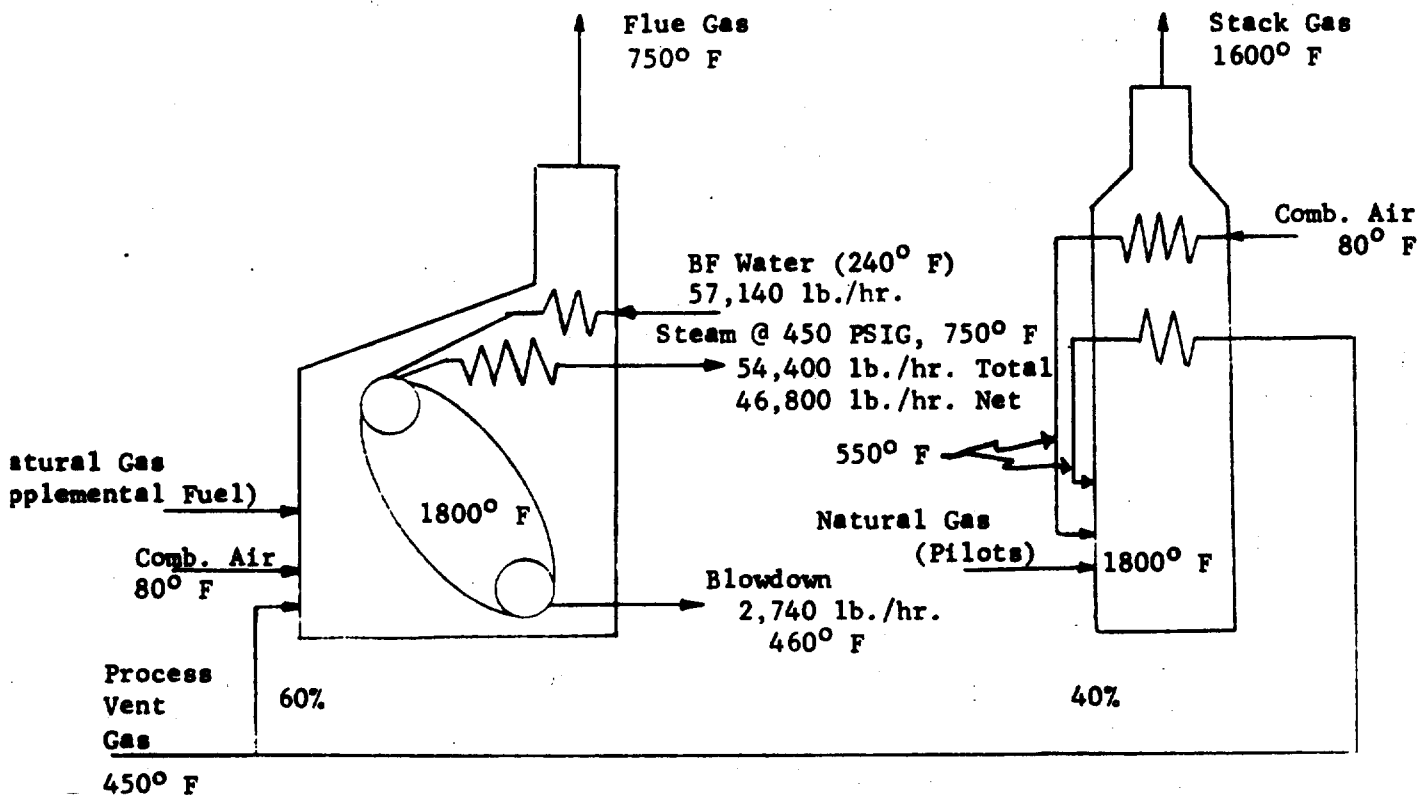
In most plants, steam utilization is limited. Hence, an economical approach to pollution control is to burn process vent gas in a thermal incinerator without supplemental fuel and pass the exhaust gases through a waste heat boiler as shown in Table CB-8. Sufficient heat is available to easily make a steam balanced operation by preheating the air in a flue gas exchanger. At least one European plant (19) is known to employ an air preheated off-gas burner for steam generation without supplemental fuel.

d. Catalytic Incineration

Table CB-9 presents a material balance for a catalytic incinerator with fresh catalyst. As the catalyst ages, combustion efficiency will decrease. With aged catalyst, it is expected that 10 to 15 percent of the feed combustibles will be vented to the atmosphere together with about 50 percent of the carbon black particulate charged to this incinerator. No existing carbon black plants are known to employ catalytic oxidation of the process vent gas. However, it has been reported that one attempt was abandoned some years ago because of catalyst poisoning. With adequate control instrumentation to prevent excessive temperatures, it should be possible to use a catalytic incinerator in this service. Based on general information for conventional catalytic incinerators in other applications, it is estimated that a 900° F inlet temperature to the catalyst bed should be sufficient to obtain complete combustion of all H_2S , hydrocarbons and carbon monoxide with standard catalysts, provided that the sulfur does not poison the catalyst. Maximum temperature within the bed should be limited to 1200° F in order to prevent loss in catalyst surface area and a resulting loss in catalyst activity. It should also be noted that SO_3 may be produced by most noble metal catalysts if the

TABLE CB-7
CO-BOILER PLUS THERMAL INCINERATOR
EMISSION CONTROL SYSTEM
90 MM LB./YR. FURNACE BLACK PLANT
OVERALL MATERIAL BALANCE, LB./HR.

<u>Component</u>	<u>Vent Gas to CO-Boiler</u>	<u>Air to CO-Boiler</u>	<u>Natural Gas to CO-Boiler</u>	<u>Flue Gas from Boiler</u>	<u>Vent Gas to Incin.</u>	<u>Air to Incin.</u>	<u>Stack Gas from Incin.</u>
H ₂	737				492		
CO ₂	5,987			21,962	3,991		13,723
CO	8,442				5,629		
H ₂ S	184				122		
S + SO ₂	TR			347	TR		231
CH ₄	191		406		127		
C ₂ H ₂	230				153		
C ₂ H ₆			89				
Carbon Black	15				9		
N ₂	54,412	66,942	42	121,400	36,274	39,421	75,696
O ₂	486	20,292		6,452	324	11,942	4,024
H ₂ O	48,134	948		57,362	32,089	558	37,450
NO _x	11			25	7		14
Total Lbs./Hr.	118,829	88,182	537	207,548	79,217	51,921	131,138
SCFM	34,440			51,000	22,960		33,000

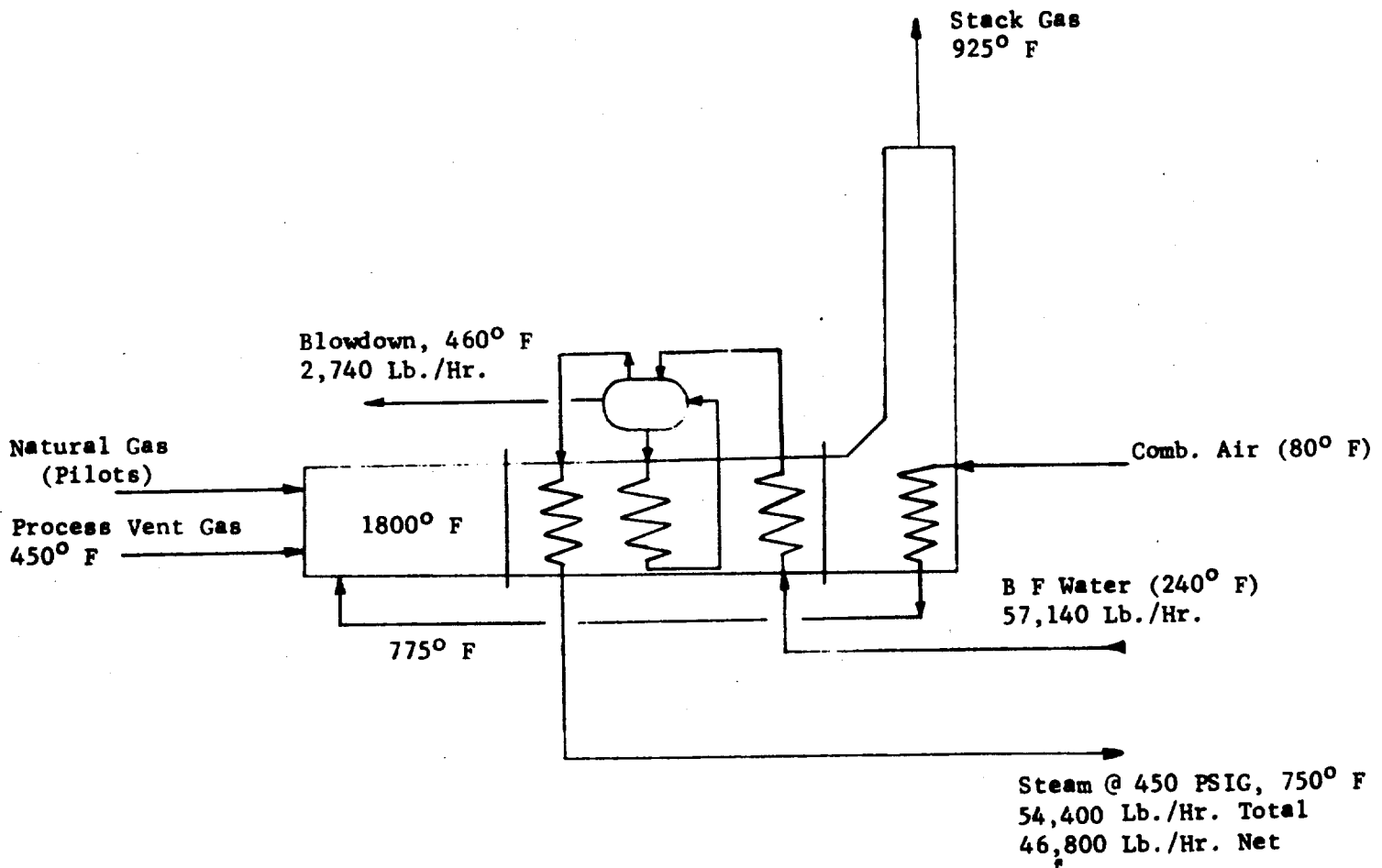


CB-49

TABLE CB-8

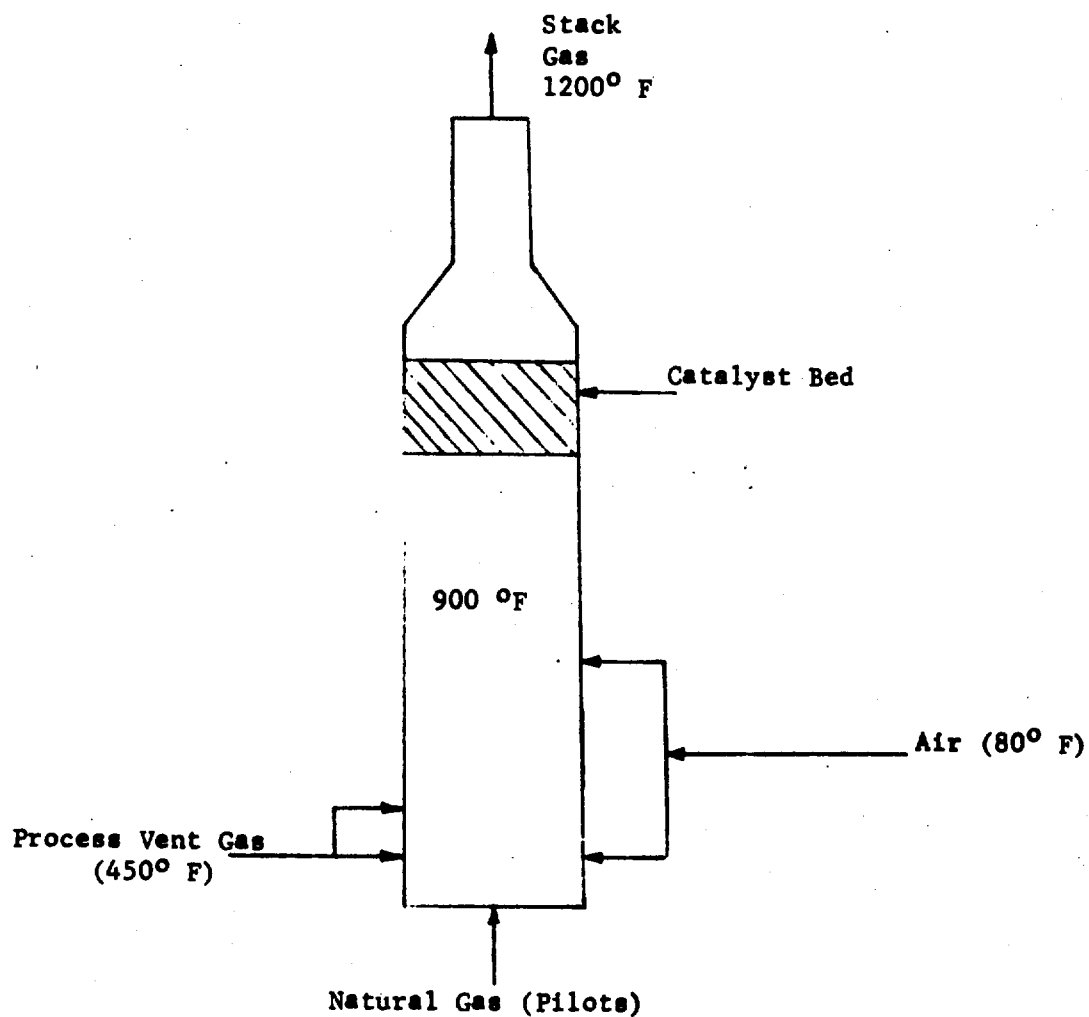
THERMAL INCINERATOR PLUS WASTE HEAT BOILER
EMISSION CONTROL SYSTEM
FOR
90 MM LB./YR. FURNACE BLACK PLANT
OVERALL MATERIAL BALANCE, LB./HR.

<u>Component</u>	<u>Process Vent Gas</u>	<u>Air to Incin.</u>	<u>Stack Gas</u>
H ₂	1,229		
CO ₂	9,978		34,308
CO	14,071		
H ₂ S	306		
S + SO ₂	TR		578
CH ₄	318		
C ₂ H ₂	383		
NO _x	18		38
Carbon Black	24		
N ₂	90,686	98,553	189,226
O ₂	810	29,848	10,060
H ₂ O	80,223	1,396	93,633
TOTAL LBS./HR.	198,046	129,797	327,843
SCFM	57,400		82,500



CB-50
TABLE CB-9
CATALYTIC INCINERATOR
FOR
90 MM LB./YR. FURNACE BLACK PLANT
OVERALL MATERIAL BALANCE, LB./HR.

<u>Component</u>	<u>Process Vent Gas</u>	<u>Air to Incin.</u>	<u>Stack Gas</u>
H ₂	1,229		
CO ₂	9,978		34,303
CO	14,071		
H ₂ S	306		
S + SO ₂	TR		578
CH ₄	318		
C ₂ H ₂	383		
NO _x	18		24
Carbon Black	24		9
N ₂	90,686	251,062	341,745
O ₂	810	76,234	56,446
H ₂ O	80,223	4,472	96,709
<hr/>			
TOTAL LBS./HR.	198,046	331,768	529,814
SCFM	57,400		127,200



temperature exceeds 750° F. These temperatures can be accomplished by permitting part of the process vent gas to by-pass the combustion zone and employing excess air as quench between combustion zone and the catalyst bed. During periods of high carbon black concentration in the incinerator feed (caused by bag filter leakage) it may be necessary to use additional quench air or to partially by-pass the catalyst bed section of the incinerator.

Sufficient heat is available in the catalytic incinerator effluent to generate a similar amount of steam in a waste heat boiler as was produced with the above thermal incinerator-boiler unit.

G. Limitations of Combustion Devices

All of the above methods of contaminant removal result in SO₂ and SO₃ production and in some cases increase NO_x content of the process vent gas. Because of the relatively low concentration level of the sulfur oxides (0.02 to 0.17 vol. % dry basis) and NO_x it would be difficult and expensive to remove these objectionable contaminants with present technology.

It should be noted that NO_x emissions shown in the material balances for the process vent gas control devices are calculated values based on published data 4,9 and thermodynamic considerations. Most of the other emissions are estimated values primarily based on general data for this type of equipment in other processing areas. This approach was necessary since several of the proposed emission control devices (waste heat boilers and catalytic incinerators) have not been employed in the carbon black industry. In addition, where the other devices have been used, the emission data are limited.

In most cases, to make practical use of the various control devices, it is necessary to collect process vent gases from many stacks into a collection header for combined processing. This results in the following:

1. Increased pressure drop which either increases system operating pressure and air blower horsepower requirement or increased size of induced draft blower.
2. Prevents a quick visual check of individual stack vent gas streams for locating leaking bag filters. With a combined vent stream feeding an efficient combustion device, considerable product could be lost before a leak would be discovered unless a photo-electric sensing device is installed up-stream of the combustion equipment. Inefficient devices such as plume burners, probably would not burn sufficient black to prevent leak detection.

H. Best Pollution Control System

Based upon the above observations and economics presented in Section VII, it appears that the most feasible air pollution control system for existing carbon black plants would include bag filters for recovery of product from process combustion vent gas and entrained carbon black from drier and product finishing vent gas streams. In addition, a plume burner or flare system, depending upon the off-gas heating value, would be used to combust burnable material in the effluent of the process vent gas filter. If the drier vent contains combustible material this stream should also be burned. This only occurs when a slip stream of process

vent gas is directly used for drying. If this stream is not used, the drier filter effluent will only contain inerts, water, CO₂ with traces of carbon black and sulfur oxides. Under these circumstances, the drier filter could be replaced with a water scrubber assuming source testing confirms the reported high efficiency of the scrubber previously described.

The most feasible air pollution control system for new plants would include the above bag filters and process vent gas thermal incinerator plus waste heat boiler with steam driven process equipment, as in Table CB-7. In either new or existing plants, if the resulting SO_x and/or NO_x content exceeds proposed emission limits, additional expensive removal facilities will be required.

All new and existing plants should have portable vacuum systems for clean-up of carbon black spills.

I. Industry Research Efforts

Current industry research effort in air pollution control centers around alternative methods of reducing the volume of vent gas which has to be processed. Methods being explored in this area include:

1. Pilot plant operation of the furnaces at increased pressure (several atmospheres) in order to reduce gas volume and provide for more efficient operation of downstream air pollution control equipment. However, as previously indicated, some operators of carbon black plants feel that reactor pressure is one of the operating variables that control the type and quality of black produced.
2. Studies of various heat exchange systems as methods of reducing direct water quench of furnace combustion products. The vent gas from a conventional carbon black unit with a minimum of indirect heat exchange contains about 45 vol. percent water. Approximately 15 percent of this water is produced in the furnace combustion. The remainder results from water quench. By eliminating this quench, the normal 30 to 50 BTU/FT.³ (wet basis) vent gas heating value could be improved, and the gas volume reduced.
3. Use of oxygen in place of air in combustion furnace. So far, reported pilot plants tests in this regard have been unsuccessful. The use of pure oxygen results in too high a flame temperature for the furnace refractory.
4. Utilization of vent gas as auxiliary feed. This has also been unsuccessful because the low heating value of the vent gas stream results in too low a flame temperature for quality blacks. By reducing water and nitrogen content of this stream by methods outlined in items 2 and 3, it may be possible to recycle the resulting vent gas. If a major portion of this gas can be recycled to the furnace, CO and hydrocarbon emissions can be reduced. However, a net vent stream is required to reject CO₂ from the system, and the quantity of sulfur in this smaller vent stream would approximate the atmospheric sulfur rejection without vent gas recycle. In most plants the normal feed gas is desulfurized

natural gas, hence, the change in total sulfur emission would be negligible. However, sulfur concentration in the net vent gas would be higher, therefore, easier and more economical to remove.

5. Work has been expended on using hydrotreated feed stocks in an effort to reduce sulfur emissions. However, hydrodesulfurized feeds are not looked upon with favor because hydrotreating lowers aromatic content. This reduction in aromatics results in lower carbon black yields per given quantity of oil feed to the reactor and also reduces the oil processing capacity of existing reactors.

V. National Emission Inventory

Based upon the emission factors shown in Table CB-3A the total approximate emissions from U. S. furnace carbon black plants are as follows:

<u>Component</u>	<u>Average Emission (b) T/T Carbon Black</u>	<u>Total Emissions (c) MM Lbs./Yr.</u>
Hydrocarbon + H ₂ S (a)	0.0519	155.7
Particulate	0.0077	8.1
NO _x	0.0023	6.9
SO _x	0.0072	21.6
CO	<u>1.2907</u> 1.3548	<u>3,872.0</u> 4,064.3

Less than 10% of the total U. S. carbon black production is produced in plants that have air pollution control devices downstream of the primary product recovery bag filters.

Assuming plume burners were used on all existing units that do not presently have process vent gas control devices, total emissions would be reduced to the following approximate values:

<u>Component</u>	<u>Average Emissions T/T Carbon Black</u>	<u>Total Emissions MM Lbs./Yr. (c)</u>
Hydrocarbon + H ₂ S (a)	0.0052	15.6
Particulate	0.0022	6.6
NO _x	0.0026	7.8
SO _x	0.0283	84.9
CO	<u>0.1374</u> 0.1757	<u>412.2</u> 527.1

It should be noted that carbon black production rate is rather constant throughout the year. As a result there is no seasonal variation in emissions.

(a) Excludes methane and hydrogen.

(b) Weighted average based on individual plant emission factors and carbon black production.

VI. Ground Level Air Quality Determination

Table CB-3A presents a summary of air emission data for the various carbon black plants. This table includes emissions from vent of process combustion products, drier exhaust, product finishing and storage area gas streams. Information regarding vapor losses from oil feed storage facilities is not included. However, emissions from this source are small since the feedstock vapor pressure is low at storage tank operating conditions (0.2 to 1.5 PSI). Product storage is normally in covered silos and hoppers which have no atmospheric loss except during loading operations.

Table CB-3A provides operating conditions and physical dimensions of the various vent stacks. The EPA will use this information together with the air emission data to calculate ground level concentrations for later reporting.

VII. Cost Effectiveness of Controls

Table CB-10 presents cost analysis for the alternate methods of reducing air pollution from the various vents. Economic data presented in this table are for a new plant producing 90 MM lbs./yr. of carbon black in multiple furnaces with three parallel trains of product recovery equipment and are based on the following:

A. Investment

Purchase cost of boilers was obtained from 1972 vendor quotes for packaged type units. Published data ⁴ were used to determine incinerator costs (packaged units). Investment data provided by carbon black manufacturers were employed to estimate installed costs for plume burners, bag filters and water scrubbers. Flare stack estimates were provided by vendors.

Installation costs for the various packaged units are estimated values based on previous experience in plant construction. A major portion of this cost represents construction labor. These costs also include providing collection headers on multiple vent streams where required.

B. Operating Expense

1. Depreciation - 10 year straight line.
2. Interest - 6% on total capital.
3. Catalyst Replacement - Based on published data ⁴, cost of catalyst for the catalytic incinerator is set at \$1,800 per thousand SCFM of gas treated, with an assumed catalyst life of two years.
4. Maintenance - Set at three percent of investment for boilers and two percent for incinerators. Maintenance costs for other control devices are based on data provided by plant operators. It should be noted that the high maintenance figures for bag filters primarily represents replacement cost of filter bags.
5. Labor - One man per shift used for direct fired boilers and six hrs./day for waste heat boilers. Virtually no operating labor is required for incinerators. Labor costs for most other units are included in the maintenance figures.
6. Utilities - Unit costs are based on typical values for the Gulf Coast area.

Except for the plume burners, all emission control devices listed require induced draft blowers. Power requirements for these blowers are based on the following assumed system differential pressures:

	ΔP in. H ₂ O
CO-boiler	14
Thermal Incinerator	6

TABLE CB-10
COST EFFECTIVENESS FOR ALTERNATE
EMISSION CONTROL DEVICES
(BASED ON 90 MM LBS./YR. CARBON BLACK PRODUCTION)

Sheet 1 of 3

Stream	PROCESS VENT GAS (a)					
	Type of Emission Control Device	CO-Boiler	Thermal Incinerator	CO-Boiler + Thermal Incinerator	Thermal Incinerator	Waste Heat
Number of Units	2	1	1	1	1	1
Capacity of each Unit, %	100	100	100	100	100	100
Feed						
Total Flow, LBS./HR.						
SCFM						
Composition, Tons/Ton Carbon Black						
Hydrocarbons (e)						
Hydrogen Sulfide						
Particulates						
NOx						
SOx						
Carbon Monoxide						
Combined Effluent						
Total Flow, LBS./HR.	345,000	327,843	327,843	327,843	327,843	327,843
SCFM	85,000	82,500	82,500	82,500	82,500	82,500
Composition, Tons/Ton Carbon Black						
Hydrocarbons						
Hydrogen Sulfide						
Particulates						
NOx	0.0031	0.0031	0.0031	0.0034	0.0008	0.0008
SOx	0.0524	0.0524	0.0524	0.0524	0.0025	0.0017
Carbon Monoxide					0.0524	0.0019
Emissions Control Efficiency						
Particulate (b)	99	99	98	100/82	63	20-30
CCR/SEER (i)	100/82	100/82	100/82	100/82	100/82	90/73
Investment, \$ (m)						
Purchased Cost	750,000	570,000	570,000	135,000	180,000 (g)	56,000
Installation	1,125,000	855,000	855,000	135,000	270,000	56,000
Total Capital	1,875,000	1,425,000	1,425,000	270,000 (d)	450,000	112,000
Operating Cost, \$/Yr. (m)						
Depreciation (10 Years)	187,500	142,500	142,500	27,000	45,000	11,200
Interest on Capital (6%)	112,500	85,500	85,500	16,200	27,000	6,700
Catalyst Replacement						
Maintenance	56,300 (3%)	42,800 (3%)	42,800 (3%)	5,400 (2%)	13,500 (3%)	2,200 (2%)
Labor \$4.85/Hr.	39,600	39,600	39,600	1,000	10,000	
Utilities						
Power, 1c/KWH						
Fuel, 40c/MM BTU (i)	57,800			2,000	8,000	
Process Water, 10c/M. Gal.				5,000	5,000	
Boiler Feed Water, 30c/M. Gal.						
Total Utilities	28,000	16,800	16,800	7,000	16,800	
Total Operating Costs	85,800	51,500	51,500	56,000	112,300	
Recovered Carbon Black, 5.5c/Lb.	481,000	361,900	361,900			
Stream Production, (c)						
On-site Usage 47c/M. Lbs.	(179,000)	(179,500)	(179,500)			
Exported, 35c/M. Lbs.	(190,900)					
Total Annual Cost	111,300	182,400	182,400	56,600 (10,600)	121,800	134,100
		209,000			33,000	134,100

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TABLE CB-10 CONT.
 COST EFFECTIVENESS FOR ALTERNATE
 EMISSION CONTROL DEVICES
 (BASED ON 90 MM LBS./YR. CARBON BLACK PRODUCTION)
 PRIOR VENT GAS

Stream	Type of Emission Control Device	Number of Units	Capacity of each Unit, %	Ray Filter		Water Scrubber		PRODUCT TRANSPORT		STORAGE	
				3	33 1/3	3	33 1/3	Ray Filter	Water Scrubber	Ray Filter	Water Scrubber
								100		1	100
Feed											
Total Flow, LBS./HR.											
SCFM											
Composition, Tons/Ton Carbon Black											
Hydrocarbons (e)								52,800		11,475	
Hydrogen Sulfide								11,500		2,500	
Particulates											
NO								0.01 ^(b)		0.0002	
SO _x											
Carbon Monoxide											
Combined Effluent											
Total Flow, LBS./HR.											
SCFM											
Composition, Tons/Ton Carbon Black											
Hydrocarbons								52,690		11,473	
Hydrogen Sulfide								11,500		2,500	
Particulates											
NO											
SO _x											
Carbon Monoxide											
Emission Control Efficiency											
Particulate (b)											
SEER (1)				99		95		99.5		90	
Investment, \$ (m)				60,000		92		99.5		90	
Purchased Cost				75,000							
Installation				135,000(£)				120,000(£)		50,000(£)	
Total Capital											
Operating Cost, \$/Yr. (m)				13,500				12,000		5,000	
Depreciation (10 years)				8,100				7,200		3,000	
Interest on Capital (6%)											
Catalyst Replacement											
Maintenance											
Labor, \$4.85/Hr.											
Utilities											
Power, 1c/KWH				1,000				1,200		300	
Fuel, 40c/MM BTU (1)											
Process Water, 10c/M. Gal.											
Boiler Feed Water, 30c/M. Gal.											
Total Utilities											
Total Operating Costs				1,000				1,200		300	
Recovered Carbon Black, 5.5c/Lb.				57,600				50,400		16,400	
Steam Production, (c)				(24,500)				(49,400)		(900)	
On-site Usage 47c/M. Lbs.											
Exported, 75c/M. Lbs.											
Total Annual Cost				33,100				1,000		15,500	

TABLE CB-10
COST EFFECTIVENESS FOR ALTERNATE
EMISSION CONTROL DEVICES
(BASED ON 90 MM LBS./YEAR CARBON BLACK PRODUCTION) Sheet 3 of 3

FOOTNOTES

- (a) Downstream of bag filter.
- (b) Expressed as (tone of particulate removed per ton of entering particulate) x 100.
- (c) 450 PSIG, 750° F steam.
- (d) Afterburner systems study by Shell Development Co. for EPA (Contract EHSD 71-3).
- (e) Excludes methane and hydrogen.
- (f) Based on investment and operating cost data provided by carbon black manufacturers.
- (g) Vendor quote.
- (h) Emission level if cyclone is employed for recovery.
- (i) Increased future fuel costs should be considered.
- (j) Not feasible with "typical" vent gas of this study, but demonstrated in certain types of operation.
- (k) Based on fuel to bring "typical" vent gas to 50 BTU/SCF.
- (l) Defined as:

$$CCR = \frac{\text{pounds of oxygen that react with pollutants in stream to the device}}{\text{pounds of oxygen that theoretically could react with these pollutants}} \times 10$$

$$SERR = \frac{\text{weighted pollutants in} - \text{weighted pollutants out}}{\text{weighted pollutants in}} \times 100$$

See Appendix for discussion and explanation.

- (m) Does not consider recent inflationary trends.

	<u>ΔP in. H₂O</u>
Thermal Incinerator plus Waste Heat Boiler	14
Catalytic Incinerator	9
Bag Filter	14
Water Scrubber	15

7. Production Credits - The value of steam used on-site has been set equal to the electric power utility costs which would apply for using motor driven equipment in the carbon black plant. The quantity of steam required on-site is based on replacing 80 percent of total power requirement with non-condensing steam turbines which exhaust to the atmosphere. The 75¢/M lb. credit used for exported steam represents a typical value for steam based on 40¢/MM BTU fuel cost. Recovered carbon black is valued at 5.5¢/lb. based on figures used by several carbon black manufacturers. This recovered material is combined with the process vent bag filter black and sent to the product finishing area.

In the cases involving CO-boilers for process vent emissions control, investment costs are based on providing two boilers each of which are able to produce the total desired steam production. Having a 100 percent spare, provides a more dependable steam supply and eliminates need for a plant shut-down during boiler inspection and maintenance.

Even if excess steam production can be utilized off-site, Table CB-10 indicates that employing dual CO-boilers is not an economical method of reducing emissions. However, if a stand-by boiler is not required and yearly boiler inspection can be handled during normal plant turn-around, a CO-boiler can be economically justified. This boiler also represents one of the most efficient methods of reducing combustible emissions.

Assuming excess steam can not be exported, the thermal incinerator followed by a waste heat boiler is the most economical processing scheme. Since waste heat boilers are somewhat more dependable than direct fired units, a single boiler should be adequate. However, if it is not desirable to shut down the whole carbon black plant once a year for boiler inspection, two 50 percent boiler facilities should be considered. No existing carbon black plant incorporates this processing scheme. However, it is assumed that process vent gas emissions from this type of unit would be similar to those predicted for CO-boilers.

Thermal incineration of the process vent gas (without steam generation) has a somewhat higher operating cost than the less efficient and less dependable plume burner. Catalytic incinerators are more expensive to operate and result in only slightly lower NO_x emissions than the thermal unit.

It should be noted that economic data presented for the various combustion devices are based on processing an average process vent gas having a heating value of 40 BTU/SCF. If for a particular grade of carbon black production, the vent gas heating value is lower than this average figure, it would be necessary to increase supplemental fuel usage in the CO-boilers and increase incinerator feed effluent heat exchange. For higher heating value gases less fuel and heat exchange are required.

Assuming reported particulate removal efficiencies are correct, Table CB-10 shows that water scrubbing of the drier vent gas is much more economical than bag filtration. Even though the water scrubber is less efficient, total particulate emissions for a plant using water scrubbers is only about 0.00025 T/T (125 lbs./hr. based on total U.S. production) more than for bag filters in this service.

If a plant incorporates pneumatic conveyor system for transporting carbon black, increased product recovery can pay for bag filter operating costs. However, this is not true for the bag filter sometimes used in product bagging and storage areas.

Costs for installing the various pollution control equipment in existing plants would be about the same or only slightly higher than the figures shown in Table CB-10. The actual cost differential would largely depend on space availability and its location relative to associated process equipment.

Obviously, with tabulations such as presented in Table CB-10, the reader can make a variety of adjustments to satisfy his own accounting techniques or technical standards. Thus, unit costs can be modified to be appropriate to local situations or to account for future or recent past escalations. Similarly, different combinations of equipment can be considered. For example, if only a single CO-boiler were employed, the investment would drop to about \$1,000,000 and the annual operating cost would become a credit of \$55,000 per year, assuming that the reliability of steam export could assure the \$190,900 estimated income.

VIII. Source Testing

It is recommended that source sampling should be performed on the CO-boiler and incinerator feed and effluent streams at the 50-26 carbon black plant. This is the only plant that employs these emission control devices and available data is limited. During sampling it would also be desirable to obtain effluent samples at reduced excess air rates (4 mol. % O₂ - dry basis) in order to confirm the somewhat more economical design basis used in the pollution control equipment economic comparison.

It is recommended that samples of the feed and effluent from drier vent gas scrubbers at plant 50-28 should be analyzed in order to determine particulate removal efficiency. If the high efficiency estimated by this carbon black manufacturer (>94% removal) can be verified by plant tests, water scrubbers could constitute an adequate substitute in this service for the much more expensive bag filters.

IX. Industry Growth Projection

The U.S. annual carbon black production (all grades) is estimated to increase to 5.5 billion pounds by 1985, see Figure CB-6.

Approximately 95 percent of all carbon black produced is used in the production of rubber. Demand in this area is strong because of the rubber industry needs for new car tires. The ratio of carbon black to rubber in tires and other rubber products continues to rise.

The projected increase in carbon black production (three percent/year) will require the construction of approximately 21 new units between 1972 and 1985, based on an average capacity of 90 million pounds per year carbon black production as used in this report. Because of the continued increase in cost of natural gas, virtually all of the new plants will incorporate the oil or mixed feed furnace process instead of the competing gas feed thermal and channel processes. It is doubtful if any existing furnace carbon black plants will be replaced during this time period. Even though the trend is toward larger plants which are somewhat more economical to operate, the smaller existing producers can improve their economics by adding parallel trains of equipment as production demands increase.

In the past, most carbon black plants were located near oil and gas feed source (i.e., Texas and Louisiana). However, recent plants have been constructed near tire manufacturers (i.e., Toledo, Ohio plus Moundsville and Waverly, West Virginia). It is expected that future plants will follow the most recent trend and be located close to the major carbon black consumers.

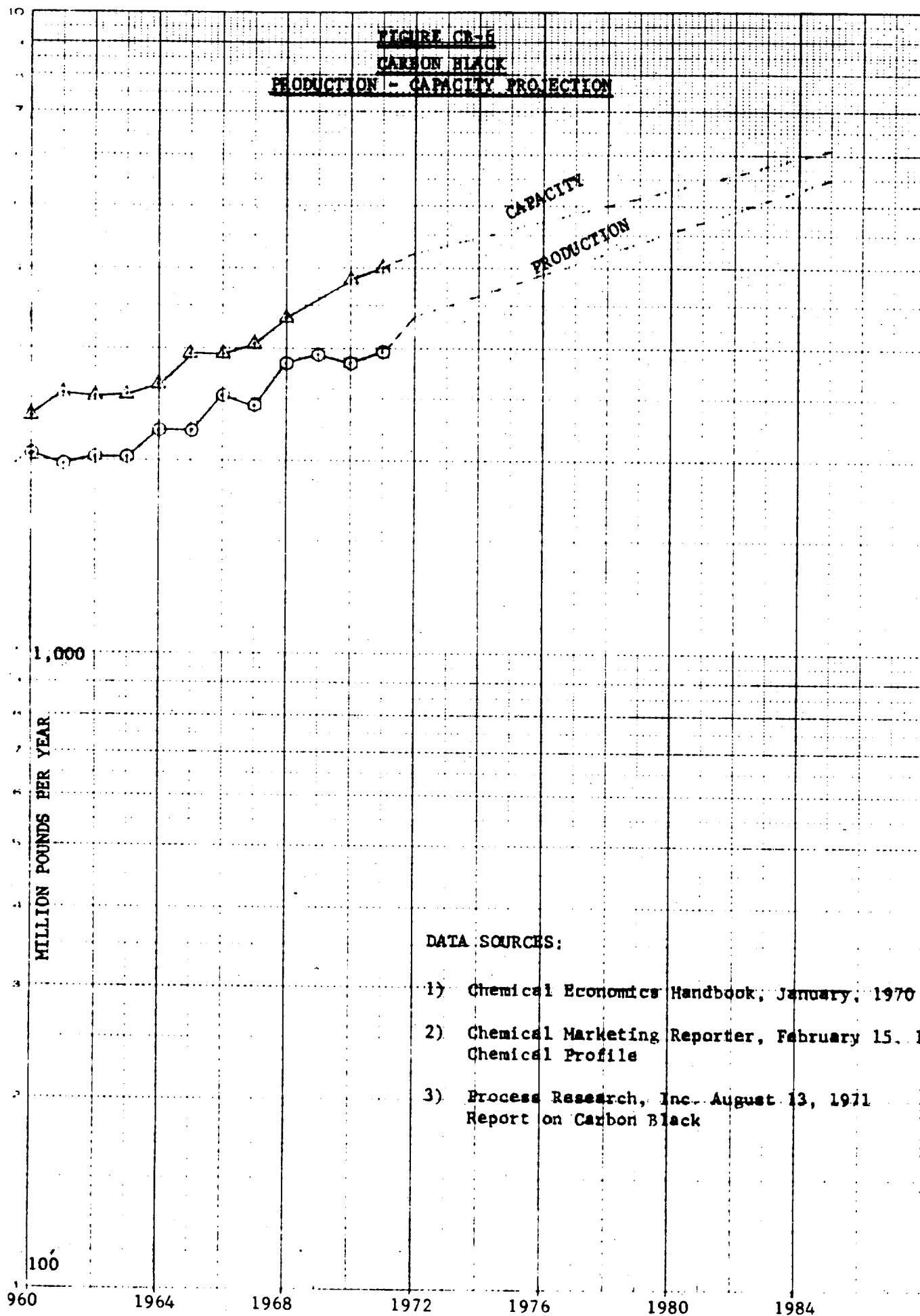
No new channel type units will be built. At present there are only two channel carbon black plants remaining in operation in the U.S. with a total installed capacity of 76 MM lbs./year. In the future these two plants, which are located in Texas, will have to operate at reduced capacity in order to meet state regulations on particulate emissions.

There are no known processes that can compete with the furnace process. Besides the high polluting channel process, the only commercially operated process for making carbon black is the thermal type unit, which presently accounts for approximately nine percent of the U.S. carbon black production. It is doubtful if the thermal process will increase its market share, because thermal blacks are large particle size carbon black which have low reinforcement and poor abrasion qualities in rubber and are, therefore, not suitable for tire tread and many other applications. In addition, this is a gas fired process which requires a high cost, short supply feedstock. Furthermore, even though the process has low CO emissions, technological problems would make clean-up of the particulates, that are emitted as puffs of smoke and flame on each furnace switch, very expensive and difficult.

At present, approximately 10 percent of carbon black produced in this country is exported. This percentage is dropping as additional plants are built abroad.

As indicated in Section II, profit margin for carbon black production is small. Therefore, any significant expenditure for air pollution control equipment could result in a higher carbon black selling price. This in turn might lead to a further decline in exports or might even result in importation of carbon black from areas where air pollution controls do not exist. If

FIGURE CB-6
CARBON BLACK
PRODUCTION - CAPACITY PROJECTION



DATA SOURCES:

- 1) Chemical Economics Handbook, January, 1970
- 2) Chemical Marketing Reporter, February 15, 1971
Chemical Profile
- 3) Process Research, Inc. August 13, 1971
Report on Carbon Black

substantial importation of carbon black does occur, the above growth projection will be reduced accordingly. At the present time, only ink grade carbon blacks are being imported because they are made chiefly by the highly polluting channel process and most U.S. channel plants have been shut down. The industry feels, however, that there is both a current and future possibility of importation of other grades, because of cost considerations.

There is no known substitute for carbon black as a filler material for tires, or as a pigment but recent improvements in cording and belting techniques could reduce demand growth rate if they result in longer tire life.

X. Plant Inspection Procedures

Loose carbon black is light and readily disperses on handling. In the various phases of production, every effort should be made at the plant to contain carbon black and prevent any loss in order to avoid air pollution.

Plant inspections will be conducted by the appropriate authorities, either on a routine basis, or in response to a complaint. Usually, the inspecting agent will only be able to make visual observations although the distinct odor of reduced sulfur compounds is sometimes experienced in the vicinity of carbon black plants that do not burn their off-gases. It is unlikely that any particulate monitoring or sampling devices will be available in the effluent streams although some plants might have provision for gas sampling.

If the inspector has any reason to suspect that emissions are excessive, some factors that he should consider and/or discuss with plants officials are itemized below:

- A. Emission of carbon black from the main process vent bag filter occurs when individual filter bags fail. When a bag fails it will tint the filter's effluent. The amount of opacity of the stack vent gas depends on the size and number of bag failures and type of emission control device downstream of the filter. A control agent should use the Ringelmann Chart to make a rough estimate of the net particulate emissions in this stream. One plant reported that during normal operations particulate emissions do not exceed 1.5 on the Ringelmann scale.

In addition to bag failures, visual discharges of particulates can be caused by improperly installed bags, loose bag clamps, or improper sealing of tube sheet joints.

If the plant is experiencing short bag life and thus frequent high emissions, it might be due to excessive pressure drop across the baghouse caused by high flow rates or other reasons (15).

Maintenance of the bag filter system is vital to its efficient operation. Therefore, many plants will keep repair and maintenance records for the baghouse and associated ductwork, fans and conveyor system.

Since it is not practical to shut down the filter system for inspection, it is necessary to know the maintenance schedule for the baghouses if the plant management is agreeable to an inspection of the inside of the filter by the control agent.

A well defined program for bag replacement based upon expected baglife helps insure proper filter operation and minimal downtime.

- B. Spillages of carbon black or losses of black to the atmosphere occur in the following processing areas:
 - 1. Around the pelleting equipment. When pellets cease to form in the dry pelleting process the drum has to be emptied, reloaded with fresh black, and reseeded before pelleting can be resumed. The emptying of the drum will result in some loss of black.

2. When cleaning the screens used to remove oversized pellets from the product before storage.
3. Whenever samples of black are drawn from various points in the production line, some dusting occurs.
4. Whenever a production line is plugged, the remedial measures can involve the use of high-pressure air to dislodge the blockage.
5. Carbon black is so finely divided that whenever a leak develops in plant equipment, black will seep out and dust into the atmosphere. These leaks, which usually develop in the conveying system, can be caused by external corrosion or internal erosion.
6. Black can seep from portions of the conveying equipment which may not be completely dust-tight due to defective seals or worn sprockets in the screw conveyor, or defective buckets in the lift elevator.
7. Black is sometimes spilled from open or torn bags in the product storage area.
8. Some loss of black to the atmosphere occasionally occurs in the packing of bags or the bulk loading of hopper cars.
9. Wastage of black occurs during the cleaning of hopper cars.
10. The cleaning of equipment being repaired will release black to the atmosphere.

A visual check of the above areas should be made to determine if adequate effort is made to minimize these sources of particulate emission and to ascertain if sufficient equipment such as portable vacuum devices and water washing facilities are available to quickly clean-up any spillage.

- C. Emissions from water scrubbers on either main process or drier vent gas streams, should be visually checked by observing the stack gas opacity after dissipation of water vapor. If excessive, it could be caused by:
1. Water pressure and flow rate to the scrubber being different than design values.
 2. Temperature and pressure of feed gas being different than plant operating and design values.
 3. Feed gas pressure drop across the scrubber being excessive.
 4. Deposits of material or internal fouling of the scrubber which could disturb flow patterns.
 5. An inadequate maintenance schedule for cleaning and replacing water nozzles.
 6. Improper operation of fans and pumps.

- D. Particulate emissions from drier and other stacks in product finishing and storage areas are normally small but should be visually checked to determine opacity. Depending upon the clean-up method employed, the above comments are applicable.
- E. If incinerators are provided on any of the vent streams, a visual check of the stack gas should be made. When smoke appears from an incinerator, malfunctioning of the combustion process or excessive leakage of an upstream bag filter should be suspected. Smoke not related to the bag filter can and should be eliminated by improving the incinerator combustion. Smoke-free combustion requires adequate time, good turbulence in mixing the fuel and air, and sufficient temperature for the reaction rate to proceed to completion and produce the desired products of oxidation. If malfunctioning of the incinerator is suspected, it could be caused by:
 - 1. Burner in combustion zone not operating. Process vent gas and/or air valves not open.
 - 2. Combustion zone temperature not in the design range.
 - 3. The quantity of excess air may be different than design. This might be determined by checking the air flow chart, or measuring the temperature of stack gases. A stack gas temperature less than design may indicate a large quantity of excess air.
 - 4. Log data on the composition of stack gas should be reviewed, if available. Variance in analytical results can usually be attributed to one or more of the aforementioned factors.

The following measures are usually recommended by manufacturers to improve performance of a smoky incinerator.

- 1. Usually smoke will be produced if the combustion zone temperature is low or fuel to air ratio is not optimal. If combustion zone temperature is low:
 - (a) Add supplemental fuel.
 - (b) Reduce the quantity of excess air if it is too high. Gaseous fuels require at most 20 percent excess air. Air requirement for liquid fuel varies between 10 to 75 percent excess, depending upon the quality of the burner. Several hundred percent excess air may be enough to chill flame and cause smoking. Caution must be taken in reducing excess air at the burner if its source is infiltration through a leaky furnace. Sealing leaks or reducing negative draft is proper method when this is the case.
 - (c) Process vent gas, fuel and air should be tested to detect abnormal water content.
- 2. If turbulence and temperature are fixed and the furnace still smokes, it may be necessary to increase the excess air flow. While low excess air flames are often desirable, the availability of additional air provides more oxygen and often results in a shorter smokeless flame.

XI. Financial Impact

Table CB-11 presents economics for carbon black manufacture in a present day typical 90 MM lbs./yr. plant that incorporates bag filters on main process and product handling vent streams, water scrubber on drier purge gas and a vacuum recovery system for clean-up of product spills. As previously indicated, estimated profit for carbon black manufacture is relatively small. Since production costs of 6.54¢/lb. are so close to selling price of 7.25¢/lb., any additional expenditures for pollution control equipment may have to be reflected in a higher carbon black selling price.

Estimated total cost for producing carbon black in this same type of existing unit, which has been modified to burn off-gas in plume burners, would be 6.58¢/lb. (see Table CB-12). This has been defined as the most feasible control method for existing plants, and results in a 5.6 percent reduction in NPAT. Table CB-12 also shows the sensitivity of the calculation to capital and operating costs for the pollution control equipment as estimated in Table CB-10. Doubling of these cost factors results in a reduction of return on investment (ROI) from 2.86 percent for the basic plant to 2.45 percent. However, total NPAT could be restored by a 1.1 percent increase in selling price.

Table CB-13 shows estimated manufacturing costs for a new most feasible type unit. This plant includes a thermal incinerator plus waste heat boiler on the combined effluent from three parallel trains of vent gas bag filters. The 46,800 lbs./hr. of superheated steam generated in the boiler is used on-site to drive process air and induce draft blowers and major pumps. Bag filters are employed on product handling and drier purge vent gas streams and in the product storage area. Total carbon black production cost for this unit would be 6.63¢/lb., resulting in a 13 percent reduction in NPAT. The sensitivity analysis shows a further decrease in ROI to 1.49 percent and the need to increase prices by 3.9 percent if total original NPAT is to be restored. It should be noted, however, that no additional steam credit is included.

Table CB-13A presents pro-forma balance sheets for the cases described above (excluding the sensitivity analyses). It was assumed in developing these asset and liability positions that management of the carbon black plant believes that the possibility of an increase in foreign imports exists, if they raise prices, and they have, therefore, chosen to accept a smaller profit margin in order to maintain sales at a peak level. Capital requirement for the most feasible new plant is about \$910,000 higher than for existing type plant.

In addition to the financial impact, one should also evaluate the overall environmental impact of the most feasible method of emission control described in this report. This, of course, is a very involved type of evaluation, but the single most important factor for consideration is the impact on the supply of energy. If, carbon black off-gases are burned and the energy value recovered and used to drive carbon black process equipment in all future plants, the energy saving will be equivalent to about eight billion standard cubic feet of natural gas per year by 1985. This would be a direct saving of natural gas if these plants are built in the Texas/Louisiana area. If, on the other hand they are built in the Ohio River Valley as seems to be the current trend, the saving would probably be in energy output from a coal burning power station thus also achieving a reduction in air pollution from that source.

TABLE CB-11
CARBON BLACK MANUFACTURING COST
FOR A TYPICAL
EXISTING 90 MM LB./YR. FACILITY

<u>DIRECT MANUFACTURING COST</u>	<u>¢/LB.</u>	<u>\$/YR.</u>
Feedstock		
Natural Gas @ 40¢/MM BTU	0.42	
Oil @ 8.0¢/Gal.	1.43	
Labor (10 men/shift @ \$4.85/Hr.)	0.44	
Maintenance (5% of invest.)	0.59	
Utilities	0.43	
	<u>3.31</u>	
<u>INDIRECT MANUFACTURING COST</u>		
Plant Overhead (110% of labor)	0.48	
Laboratory	0.24	
	<u>0.72</u>	
<u>FIXED MANUFACTURING COST</u>		
Depreciation (10 years)	1.19	
Insurance & property taxes (2.3% of invest.)	0.27	
	<u>1.46</u>	
<u>MANUFACTURING COST</u>	5.49	
<u>GENERAL EXPENSES</u>		
Administration (3% of manufacturing cost)	0.17	
Sales (1% of manufacturing cost)	0.06	
Research (2% of manufacturing cost)	0.11	
Finance (6% of investment)	0.71	
	<u>1.05</u>	
Total Cost	6.54*	5,886,000
Selling price	7.25*	6,525,000
Profit before taxes		639,000
Profit after 52% tax (NPAT)		306,700
Cash flow		1,377,700
ROI (NPAT x 100/Investment)		2.86%
*Based on bulk rate. If sold in bags, manufacturing cost and selling price 0.75¢/lb. higher.		

TABLE CB-12
CARBON BLACK MANUFACTURING COST
FOR A TYPICAL
EXISTING 90 MM LBS./YR. FACILITY WITH
RETROFIT PLUME BURNER

<u>DIRECT MANUFACTURING COST</u>	<u>¢/LB.</u>	<u>\$/YR.</u>
Feedstock		
Natural Gas @ 40¢/MM BTU	0.42	
Oil @ 8.0¢/Gal.	1.43	
Labor	0.44	
Maintenance	0.60	
Utilities	<u>0.43</u>	
	3.32	
<u>INDIRECT MANUFACTURING COST</u>		
Plant Overhead (110% of labor)	0.48	
Laboratory	<u>0.24</u>	
	0.72	
<u>FIXED MANUFACTURING COST</u>		
Depreciation (10 years)	1.21	
Insurance & property taxes (2.3% of invest.)	<u>0.27</u>	
	1.48	
<u>MANUFACTURING COST</u>	5.52	
<u>GENERAL EXPENSES</u>		
Administration (3% of manufacturing cost)	0.17	
Sales (1% of manufacturing cost)	0.06	
Research (2% of manufacturing cost)	0.11	
Finance (6% of investment)	<u>0.72</u>	
	1.06	
Total Cost	6.58*	5,922,000
Selling price	7.25*	6,525,000
Profit before taxes		603,000
Profit after 52% tax (NAPT)		289,400
Cash flow		1,378,400
ROI (NPAT x 100/Investment)		2.66%

*Based on bulk rate. If sold in bags, manufacturing cost and selling price 0.75¢/lb. higher

	<u>Sensitivity Analysis (100% increase in:)</u>	
	<u>Capital Charges</u>	<u>Capital Charges plus Utility Costs</u>
NPAT, \$/Yr.	272,400	271,900
Cash Flow, \$/Yr.	1,376,400	1,375,900
ROI, %	2.46	2.45

TABLE CB-13
CARBON BLACK MANUFACTURING COST
FOR A MOST FEASIBLE NEW
90 MM LBS./YR. FACILITY
WITH INCINERATOR & WASTE HEAT BOILER

<u>DIRECT MANUFACTURING COST</u>	<u>c/LB.</u>	<u>\$/YR.</u>
Feedstock		
Natural Gas @ 40¢/MM BTU	0.42	
Oil @ 8.0¢/Gal.	1.43	
Labor	0.45	
Maintenance	0.64	
Utilities	0.25	
	3.19	
<u>INDIRECT MANUFACTURING COST</u>		
Plant Overhead (110% of labor)	0.50	
Laboratory	0.24	
	0.74	
<u>FIXED MANUFACTURING COST</u>		
Depreciation (10 years)	1.29	
Insurance & property taxes (2.3% of invest.)	0.30	
	1.59	
<u>MANUFACTURING COST</u>	5.52	
<u>GENERAL EXPENSES</u>		
Administration (3% of manufacturing cost)	0.17	
Sales (1% of manufacturing cost)	0.06	
Research (2% of manufacturing cost)	0.11	
Finance (6% of investment)	0.77	
	1.11	
Total Cost	6.63*	5,967,000
Selling price	7.25*	6,525,000
Profit before taxes		558,000
Profit after 52% tax (NPAT)		267,000
Cash flow		1,428,000
ROI (NPAT x 100/Investment)		2.30%

*Based on bulk rate. If sold in bags, manufacturing cost and selling price 0.75¢/lb. higher.

Sensitivity Analysis (100% increase in:)
Capital Charges Capital Charges plus Utility Costs**

NPAT, \$/Yr.	195,500	184,000
Cash Flow, \$/Yr.	1,428,500	1,417,000
ROI, %	1.59	1.49

**Excludes additional credit for steam at escalated cost rates.

TABLE CB-13A
PRO-FORMA BALANCE SHEET
90 MM LB./YR. CARFON BLACK MANUFACTURING FACILITY

	Existing	Existing with Plume Burner	Most Feasible New
Current Assets			
Cash (A)	\$ 411,750	\$ 414,000	\$ 414,000
Accounts Receivable (B)	543,750	543,750	543,750
Inventories (C)	654,000	658,000	663,000
Fixed Assets			
Plant	10,710,000	10,860,000	11,575,000
Buildings	100,000	100,000	100,000
Land	50,000	50,000	50,000
Total Assets	<u>\$12,469,500</u>	<u>\$12,625,750</u>	<u>\$13,345,750</u>
Current Liabilities (D)			
Equity & Long Term Debt	\$ 327,750	\$ 328,500	\$ 320,250
	<u>12,141,750</u>	<u>12,297,250</u>	<u>13,025,500</u>
Total Capital	<u>\$12,469,500</u>	<u>\$12,625,750</u>	<u>\$13,345,750</u>

(A) Based on one month's total manufacturing cost.

(B) Based on one month's sales.

(C) Based on 10 MM Lbs. of product valued at total cost.

(D) Based on one month's total cost less fixed manufacturing and finance costs.

XII. Cost to Industry

In the typical present day plant depicted in Table CB-11 approximately 5% of the plant investment cost is directly attributed to air pollution equipment. This expenditure plus associated operating costs equals 2% of the carbon black total production cost (0.13 ¢/lb.). Included in this expenditure are the following items:

- A. Approximately 10% of the process vent gas bag filter investment. The remaining cost of this facility is assumed to represent normal process requirements for product recovery.
- B. Additional concrete surfacing in plant area. This facilitates clean-up of carbon black spills.
- C. Vacuum clean-up system.
- D. Net expenditures for product transport bag filter and drier vent gas water scrubber.

As noted in Section XI, the proposed most feasible modification of existing carbon black plants results in only a slight increase in production cost (0.04 ¢/lb.). Even with the existing low profit margin, it is doubtful if this cost increase should cause any significant economic problems to the industry.

Assuming all existing U. S. furnace black plants without process vent gas incineration are modified to incorporate plume burners, the total investment for this conversion would be approximately \$5,000,000.

In the "most feasible new plant" presented in Table CB-13, air pollution control equipment represents approximately 12% of total capital and 0.22 ¢/lb. of the carbon black production cost. The resulting 0.09 ¢/lb. higher cost than for the present day typical unit, in all likelihood, will not reduce growth in demand for carbon black but could increase demand for foreign produced black.

Assuming all new plants built between now and 1985 incorporate this type of air pollution control equipment, the total incremental capital cost will be about \$18,000,000.

The projected effect of the above expenditures on future air emissions is shown in Table CB-14.

TABLE CB-14
ESTIMATED 1985 AIR EMISSIONS
FOR
ALTERNATE CONTROL SYSTEMS

Type of Pollution Control Carbon Black Production, (A) Tons/Yr.	Typical Present System 2,500,000				Most Feasible Modified Existing Plant (C) 2,500,000				Most Feasible Modifications (D)					
									Existing Plants		New Plants			
	Average Emissions T/T	Total Emissions MM Lbs./Yr.	Weighted Emissions		Average Emissions T/T	Total Emissions MM Lbs./Yr.	Weighted Emissions		Average Emissions T/T	Total Emissions MM Lbs./Yr.	Average Emissions T/T	Total Emissions MM Lbs./Yr.	Total Emissions MM Lbs./Yr.	Weighted Emissions
Pollutant														
Hydrocarbons + H ₂ S	0.0519 = $\frac{6453.5}{124,000}$	259.5	20,760		0.0052	26.0	2,080		0.0052	15.6	0.0052	15.6	15.6	1,250
Particulate	0.0027	13.5	810		0.0022	11.0	660		0.0022	6.6	0.0022	6.6	6.6	400
NO _x	0.0023	11.5	460		0.0026	13.0	520		0.0026	7.8	0.0042	8.4	16.2	650
SO _x	0.0072	36.0	720		0.0283	141.5	2,830		0.0283	84.9	0.0307	61.4	146.3	2,930
CO	1.2907	6,453.5	6,450	(B)	0.1374	687.0	690		0.1374	412.2	0.0349	69.8	412.2	410
	1.3548	6,774.0	29,200		0.1757	878.5	6,780	(B)	0.1754	527.1	0.0349	69.8	596.9	5,640 (B)

CB-75

- A. By furnace process.
- B. Significant Emission Index, which is based on the following weighting factors:
Hydrocarbon = 80, Particulate = 60, NO_x = 40, SO_x = 20 and CO = 1. (See Appendix for discussion and explanation.)
- C. Assumes all existing plants modified and new plants built to incorporate plume burners and other pollution control devices used in Table CB-12.
- D. All existing plants modified to incorporate plume burners and new plants based on thermal incineration plus WHB and other pollution control devices used in Table CB-13.

XIII. Emission Control Deficiencies

Technical deficiencies preventing reduced levels of emissions include the following:

A. Process Chemistry and Kinetics

Production of carbon black is a non-catalytic partial oxidation reaction. The quantity and type of carbon black produced is influenced by feedstock quality, oxygen concentration in reactor furnace plus reactor residence time and operating temperature.

1. Feedstock

All liquid feeds presently employed contain sulfur, most of which is ultimately vented to the atmosphere as H_2S or sulfur oxides. Based on present technology it is not possible to desulfurize the feed without some reduction in aromatic content which results in lower carbon black yield.

2. Oxygen Concentration

All existing carbon black plants use air as a source of oxygen. This results in a large volume of nitrogen being vented which dilutes other emissions. Because of this dilution, it is more difficult and expensive to control the quantity of these emissions.

3. Reactor Operating Conditions

Reactor operating conditions influence the quantity of non-selective products obtained. However, since physical properties of the carbon black are also related to the operating conditions, temperature and other operating variables can not be arbitrarily adjusted to limit emissions.

B. Process Equipment and Operations

1. Reactor Furnace

Each major carbon black producer has its own reactor furnace and burner design.⁵ The design of this equipment does effect carbon black selectivity to a certain extent but general magnitude of emissions for all commercial reactors are similar.

2. Quench System

A major portion of the heat of reaction is lost in the effluent water quench. In addition to wasting energy this quench water increases volume of the vent stream.

C. Control Equipment and Operations

The proposed treatment scheme, involving incineration of the exhaust from a bag filter, is the best method of reducing organics and residual carbon to negligible quantities. The deficiency in this treatment scheme is that it does not remove sulfur compounds or nitrogen oxides generated in the manufacturing process. In fact, nitrogen and sulfur oxides are generated as a result of the incineration.

If these emissions exceed future air pollution limits, additional treatment of flue gas for removal of contaminants would be required. Unfortunately, application of the few available treatment methods have not been technically and economically developed on a commercial scale. Some of these methods are:

1. Stone & Webster ¹² - Ionics Process is a commercial method to remove SO_2 . The process includes a sulfur dioxide scrubber in which SO_2 is absorbed in a sodium hydroxide solution.
2. A number of processes have been developed using liquid absorption techniques for removing SO_2 but most are not very practical ¹³. For instance; (a) sulphidine process uses a mixture of xylidine and water in approximately 50-50 percent mixtures and the by-products are sodium sulfate and SO_2 , (b) the ASARCO process developed by American Smelting & Refining Co. for the removal of SO_2 uses dimethylamine as the absorbant, (c) SO_2 is often absorbed by aqueous ammonia to produce ammonia sulfite, with subsequent oxidation to sulfate.
3. Flue Gas Cleaning: Combustion Engineering's ¹⁴ Limewater - SO_2 Scrubbing Process is a commercial flue gas cleaning process that has been reported to remove oxides of sulfur and nitrogen. Slaked lime or limestone aqueous suspensions, which are capable of removing SO_2 or SO_3 as acid gases, are capable of removing a certain amount of NO_x for the same reason. However NO_x removal from stack gases is more difficult. Other flue gas treating processes under study for SO_2 control that have shown varying abilities to remove NO_x are the Reinluft Char Process and the Tyco Laboratories Modified Lead Chamber Process ¹⁴. These processes are still in the research stage.
 - (a) Reinluft Char Process: This process uses a slowly moving bed of activated char to remove primarily the sulfur oxides from flow gases. Some NO_x may simultaneously be removed.
 - (b) Tyco Laboratories; Modified Lead Chamber Process: This flue gas treating process being researched by Tyco Laboratories, Inc., under contract to NAPCA, utilized the chemistry of the chamber sulfuric acid process to remove both sulfur and nitrogen oxides.
 - (c) Catalytic reduction of oxides of nitrogen is also reported to be in the development stage.

XIV. Research and Development Needs

If the technology deficiencies discussed under Section XIII are to be overcome, additional R & D is desirable in the following areas:

A. Existing Plants

1. Feedstock Desulfurization

It would be desirable to develop a method of desulfurizing the feed without saturating aromatics. However, it is not believed that R & D in this area can be justified at this time. Other much larger industries, such as the petroleum refiners and utility companies, are spending large sums of money in desulfurization technology and possible future developments in this effort can find application in carbon black manufacture.

If full range crude oil is desulfurized before further processing, the conventional high aromatic carbon black feedstocks would contain less sulfur compounds. However, based on present technology and air pollution laws, it is not economical or necessary to desulfurize full range crude. Many products derived from crude oil can be produced without desulfurization. In addition, with present technology it is not possible to completely desulfurize the high boiling crude fractions. Since carbon black manufacture consumes only a very small percentage of the petroleum production, it is not possible to justify crude oil desulfurization R & D for this particular application. However, if a technology break-through or air quality controls make crude oil desulfurization practical, then tests on carbon black feeds derived from desulfurized crude should be made.

2. Oxygen Feed plus Vent Gas Recycle

A combination of pure oxygen feed in place of air and recycle of vent gas to the reactor furnaces could possibly overcome problems previously experienced in efforts to reduce net emissions.

B. New Plants

In addition to the above R & D areas which have application to both new and existing plants, the following items would require new facilities for utilization of gained technology:

1. Substitute Feeds

In the furnace carbon black process, feedstock costs represent 25-30% of the manufacturing cost. Any possible reduction in this particular cost item could help defray the cost of future pollution control devices. One possibility in this area could be used tires as a substitute feedstock. Tire casings could conceivably be distilled and the aromatic liquid used as feed in a conventional type reactor or the casings directly charged to the carbon black furnace. For the latter approach, the furnace design would have to include provision for solid waste rejection. Before any R & D effort is expended in this regard, a study of logistics is necessary in order to determine if adequate feed would be available. By converting tires to a liquid feed, logistics are not as critical, since the

distillation facilities would not have to be located at the carbon, black plant site. However, in any case, since sulfur is added to rubber during its formulation, the possibility of pollution from this source will require consideration.

2. Modified Processing Scheme

R & D might show that the "checker" brick furnace used in the thermal carbon black manufacturing process could have application in a mixed feed operation. It may be possible to replace part of the natural gas feed normally used in the thermal reactor with oil and thereby produce carbon black at high selectivity with low average gaseous emissions which is indicative of the thermal process. However, even with redesign of the "checker" furnace it is very doubtful if small particle size product can be obtained by this modified thermal process.

XV. Research and Development Programs

Of the various R & D project areas listed in Section XIV, only one appears to have a good chance of success for obtaining a method of reducing emissions from future carbon black manufacture. A proposed R & D program for scoping this project is as follows:

1. Project Title - Oxygen Feed plus Vent Gas Recycle for Reduced Emissions.

2. Object

To develop preliminary data on a modified furnace black process which could result in vent stack gas emissions significantly lower than the present processing scheme.

3. Project Cost (see Table CB-15 for cost breakdown)

Capital Expenditures	\$275,000
Operating Costs	
Total Manpower	148,600
Services	12,100
Materials	7,500
Contingency	48,800
Total	<u>\$492,000</u>

4. Scope

On a laboratory scale, modify the furnace black process by recycling stack gas so that contained combustibles can replace part of normal fuel requirements. By employing this low heating value fuel, it should be possible to use pure oxygen in place of most if not all of the air presently used for combustion. In addition to reducing the total volume of net emissions, less NO_x will be formed in the furnace reactor because of the reduction or complete absence of nitrogen.

5. Program

(a) Engineering

Process engineering effort is required to determine if thermodynamic equilibrium favor recycle of vent gas as a method or reducing net emissions. In addition, engineering studies will determine if it is economically desirable to cool the recycle gas for water removal.

(b) Design, Construction and Checkout

This part of the project is concerned with the design, fabrication and/or purchase of equipment and start-up of a laboratory-scale pilot plant. The furnace is the heart of the process. Since carbon black furnace design is still largely empirical, the pilot plant reactor should be designed to allow as much control as possible over temperature, turbulence and residence time.

(c) Feasibility Demonstration

This part of the project calls for operating the unit in the

TABLE CB-15
DETAILED COSTS
FOR
R & D PROJECT

Engineering

Process Design

Process Engineer, 2 Men - 16 Weeks (Each) 19,500

Contingency 2,500

22,000

Design, Construction & Checkout

Design Manpower: Professional - 16 Weeks 14,800

Major Equipment, Installed 275,000

Contingency 30,200

320,000

Feasibility Demonstration

Operation

Manpower: Professional 4.0 Weeks 3,700

Technician - 2 Men/Shift, 3 Shifts/Day for 8 Weeks 34,400

Services: Analytical - 300 Hours 4,400

Materials 2,500

Contingency 5,000

50,000

Process Development

Operation

Manpower: Professional - 8.0 Weeks 7,400

Technician - 2 Men/Shift, 3 Shifts/Day for 16 Weeks 68,800

Services: Analytical - 500 Hours 7,200

Computational 500

Materials 5,000

Contingency 11,100

100,000

conventional manner; i.e., with air and without recycle, to demonstrate that the unit can produce carbon black. Carbon quality would be gauged by simple analytical tests for tint values, iodine number and oil absorption as measures of particle size, surface area and structure, respectively. In addition an electron microscope would be used to examine particle structure.

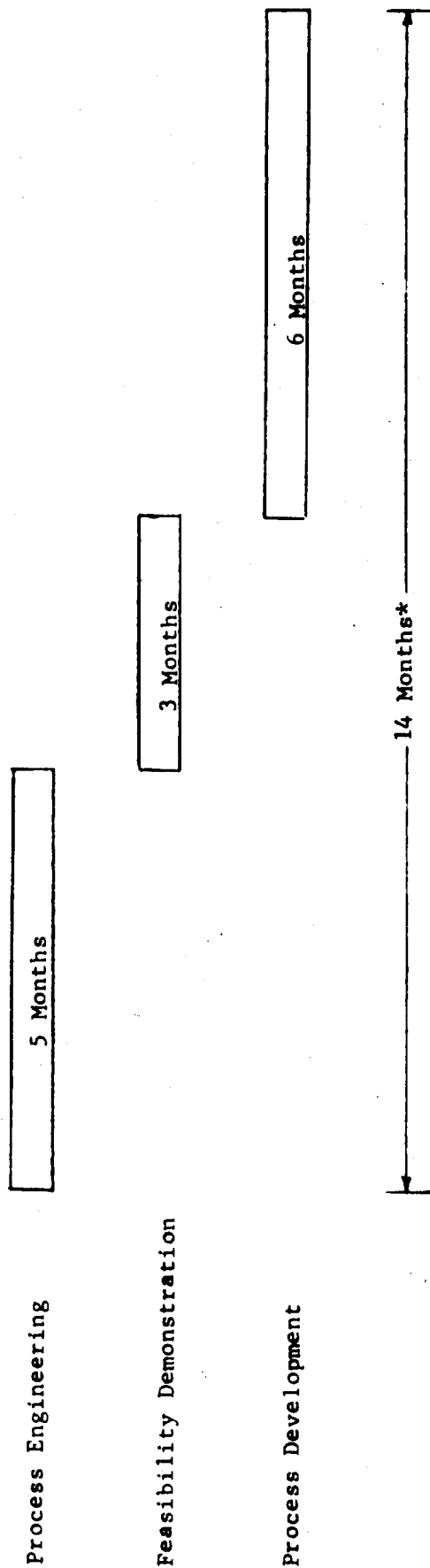
(d) Process Development

Process development work actually begins at this point in the project. It is expected that a process variables study might find a set of operating conditions which would yield carbon black of commercial quality. Pure oxygen is to be mixed with steam plus CO and CO₂ (composition adjusted to approximate equilibrium operation). As a starting point, quantity of synthetic gas and oxygen is to be adjusted to duplicate reactor residence time and oxygen partial pressure employed in successful feasibility run. After general scoping runs the pilot unit would be switched to recycle operation. Again carbon quality would be gauged by relatively simple analytical techniques. If any extremely promising carbon black samples are obtained, they should be sent out to be blended into rubber batches and tested for physical properties.

6. Timetable

Total time for project is estimated to be 14 months (excludes time required for delivery and construction of pilot plant equipment). Figure CB-7 presents a bar graph for the proposed work schedule.

FIGURE CB-7
CALENDAR TIME SCHEDULE
 FOR
R & D PROJECT



*Excludes time required after process engineering studies for procurement and construction of pilot plant equipment.

XVI. Sampling, Monitoring and Analytical Methods for Pollutants in Air Emissions**A. Methods in Use for Gaseous Pollutants**

In the carbon black industry, gaseous pollutants resulting from the reducing-flame combustion of hydrocarbon fuels may be categorized as combustion products, sulfur compounds and oxides of nitrogen. The combustion products category includes hydrogen, carbon monoxide, carbon dioxide, methane, acetylene and gases normally found in the atmosphere. The sulfur compounds measured consist of a mixture of hydrogen sulfide and sulfur dioxide, although some free sulfur may also be present in the stack gases. The oxides of nitrogen result from combustion and probably consist principally of nitric oxide.

Six replies were received in response to an inquiry relating to methods for sampling and analysis of combustion products. The quality of response was quite varied, necessitating follow-up of most responses. The information obtained is summarized in Table CB-16. It may be seen that gas chromatography is the universal analytical tool with double or triple columns indicated in most replies. The frequency of analysis was related to production control requirements and ranged from daily to semi-annually.

From the air pollution standpoint, the principal gaseous components of interest are carbon monoxide and acetylene. The analytical method of multi-column gas chromatography is an entirely acceptable technique for isolation of CO and C₂H₂ from a gas mixture. Some questions, however, might be raised concerning possible losses in the moisture removal step or through reaction in the sample container. Although preference might be given to inert gas dilution instead of condensation for moisture control, the low solubility of acetylene and the short reaction time in the case of carbon monoxide would probably minimize any errors. Assuming that the samples are analyzed immediately following collections, it is probable that the results obtained adequately reflect the true emissions and further work in methods development is not warranted.

A variety of methods for the analysis of sulfur dioxide and hydrogen sulfide were indicated by the four responses received. These are summarized in Table CB-16. Two plants use a single train containing peroxide impingers for SO₂ and cadmium sulfate impingers for H₂S.¹⁶ One plant reported the determination of total sulfur by material balance with SO₂/H₂S ratio measured by gas chromatography. The fourth plant reported the determination of SO₂ and H₂S by gas chromatography with an SO₂ check using a modified West-Gaeke procedure.¹⁷ The frequency of analysis was low in all cases (typically once per year).

The principal criticisms of the methods listed related to the possible occurrence and behavior of free sulfur in the gases and sample train and to the plausibility of the existence of SO₂ and H₂S in near equal quantities.

Based upon thermodynamic equilibrium calculations, the quantity of sulfur present as elemental sulfur and SO₂ would be expected to be very small.

Any free sulfur passing the filter in the impinger trains might inflate the SO₂ results or the oxidation of H₂S in the peroxide impingers might produce the same result. This effect, however, would not occur in the gas

chromatography technique unless sulfur or hydrogen sulfide is oxidized to SO_2 in the sample collection bottle. The latter possibility appears remote since the production of sulfur from SO_2 and H_2S would be the expected reaction.

Sufficient information is not available for a precise critique of the methods presented, but the compatibility of results produced by four divergent techniques would tend to indicate that the methods are probably free of major error. Of the methods described, it appears that the material balance combined with gas chromatography offers the greatest potential if it could be shown that sulfur is not present in the stack gases. It should be noted that virtually no manufacturer has been able to close the overall plant sulfur balance.

Only one plant analyzed for total oxides of nitrogen (Table CB-16) using a pair of small impingers containing peroxide for collection and the phenoldisulfonic acid technique for analysis¹⁶. Insufficient detail was furnished for a precise evaluation of the technique, but collection efficiency might be low and somewhat variable and there may be interferences due to the complex gas stream components. Considering the single measurement reported, it appears that further NO_x emission data should be developed. Since the gas stream is quite complex, chemiluminescence would be the best method of analysis.

Two plants reported particulate samples using the Alundum thimble and stainless steel train¹⁷. Several possible deficiencies are inherent in this technique, including the questionable efficiency of the thimble on the small carbon black particles and possible reaction of the gas mixture on or with the stainless steel portions of the train. One plant reported the reaction of H_2S and SO_2 in a stainless sample bottle to form free sulfur. Insufficient information is available for a precise critique, but it appears that the reported results are subject to significant error. Further sampling should be undertaken using an EPA train¹⁸ with high efficiency glass fiber filter and glass components.

B. Recommendations for Methods Development

1. No further work is necessary for combustion gas analysis (including carbon monoxide and acetylene).
2. A limited literature review revealed no information on the analysis of mixtures of sulfur dioxide, elemental sulfur and hydrogen sulfide. Development work is required to determine first whether the mixture actually exists in the stack gases and second, to find suitable collection techniques that will permit separation and analysis of the components without interaction.
3. The survey revealed little information on oxides of nitrogen emissions, but from the standpoint of methodology, it appears that chemiluminescence should be applicable without further development.
4. The EPA sampling train and technique should be applicable to carbon black measurement, but some consideration should be given to the question of possible reaction of H_2S and SO_2 in the train to produce solid sulfur.

TABLE CB-16
SUMMARY OF
SAMPLING AND ANALYTICAL METHODS REPORTED
FOR POLLUTANTS

Sheet 1 of 3

<u>Component</u>	<u>Method No.</u>	<u>Procedure</u>
Combustion Products (H ₂ , CO, CO ₂ , CH ₄ , C ₂ H ₂ , N ₂ , A, O ₂)	1	Collect gases in glass sample bottle after passing through anhydrous scrubber for water removal. Analysis by double column gas chromatography H ₂ , O ₂ , N ₂ , CH ₄ on 5A molecular sieve using argon carrier. CO ₂ , C ₂ H ₂ , C ₂ , C ₃ , etc. on Porepak Q using helium carrier.
	2	Sample train consisting of metal filter, cooling coil, knockout pot, pump and stainless steel pressure cylinder. Analysis of H ₂ , A + O ₂ , CO ₂ , N ₂ , C ₂ H ₂ , CH ₄ and CO by double column gas chromatography. CO ₂ and C ₂ H ₂ on charcoal column with silicate solution. Others on 5A molecular sieve.
	3	Filter and analyze using gas chromatography.
	4	Pump sample into glass tube. Analyze using gas chromatography
	5	Analysis by gas chromatography.
	6	Analysis by Orsat and gas chromatography. Columns consist of: 30% 2 ethyl hexosilicate on 60-80 mesh chromosorb P; 5' x $\frac{1}{4}$ " stainless column containing 45-60 mesh chromosorb P; and 7' x $\frac{1}{4}$ " stainless column with 13x molecular sieve.
Sulfur dioxide	1	Collect in 3% peroxide contained in a series of 2 ASTM D 1266 lamp sulfur absorbers. Precipitate with BaCl ₂ and filter through Whatman # 42 filter paper. Place filter into burned and tared thimble. Dry and ignite paper in thimble using Bunsen burner. Burn thimble in muffle furnace at 950° C for 2 hours. cool and weigh. 16
	2	Sintered metal filter followed by 2 impingers each containing

TABLE CB-16 (continued)

Sheet 2 of 3

<u>Component</u>	<u>Method No.</u>	<u>Procedure</u>
		100 ml. of 3% H ₂ O ₂ . Measured volume of impinger contents and withdraw a 5 ml. aliquot. Add 20 ml. isopropyl alcohol and 6 drops thorin indicator. Titrate with 0.01 N BaCl ₂ to endpoint. ¹⁶
	3	Determine total sulfur by material balance. Determine split between H ₂ S and SO ₂ by gas chromatography.
	4	Sulfur dioxide determined using both a modified West-Gaeke procedure and by gas chromatography. The G-C column is 6' stainless containing 15% Yukon LB 550 x on 60-80 mesh chromosorb P-AW-BMCS. The column is operated at 54° C using a helium carrier.
Hydrogen Sulfide	1	Collect in a series of 2 impingers containing a total of 200 ml. CdSO ₄ . Impingers follow the SO ₂ train described as method 1 above. The impingers are made from 38 mm x 200 mm test tubes with rubber stoppers and drawn glass tubing. The impinger contents are washed through a tared filter crucible dried on a hotplate and heated for 2 hours in an oven at 550° C. The crucible is cooled and weighed. ¹⁶
	2	Two impingers containing a total of 250 ml. 5% CdSO ₄ are placed behind the SO ₂ impingers described as method 2 above. Measure volume of impinger contents and add suitable aliquot of iodine solution. Titrate excess iodine with sodium thiosulfate solution using a starch indicator. ¹⁶
	3	Determine total sulfur by material balance. Determine split between H ₂ S and SO ₂ by gas chromatography.
	4	Hydrogen sulfide measured along with SO ₂ using gas chromatography. The G-C column is 6' stainless containing 15% Yukon LB550 x on

TABLE CB-16 (continued)

Sheet 3 of 3

<u>Component</u>	<u>Method No.</u>	<u>Procedure</u>
		60-80 mesh chromosorb P-AW-BMCS. The column is operated at 54° C using a helium carrier.
Oxides of Nitrogen	1	Sample collected in a series of 2 impingers fabricated from 4 oz. bottles with rubber stoppers and drawn glass tubing. Each impinger contains 50 ml. 3% peroxide solution. Collect a suitable sample at 0.075 cfm. Let stand overnight and analyze using the phenoldisulfonic acid technique described in "Atmospheric Emissions from Sulfuric Acid Manufacturing Processes". ¹⁶
Particulates	1	Equipment and technique described in Bulletin WP-50 ¹⁷ , Alundum thimble filtration and isokinetic sampling based on calculated sampling rate.
	2	Isokinetic sampling based on an Alundum thimble and stainless steel train. Western Precipitation equipment implied. ¹⁷

XVII. Emergency Action Plan (EAP) For Air Pollution Episodes

A. Types of Episodes

Alleviation of Air Pollution Episodes as suggested by the U.S. Environmental Protection Agency is based on a pre-planned episode emission reduction scheme. The criteria that set this scheme into motion are:

1. Alert Status - The alert level is that concentration of pollutants at which short-term health effects can be expected to occur.
2. Warning Status - The warning level indicates that air quality is continuing to deteriorate and that additional abatement actions are necessary.
3. Emergency Status - The emergency level is that level at which a substantial endangerment to human health can be expected. These criteria are absolute in the sense that they represent a level of pollution that must not be allowed to occur.

B. Sources of Emission

As outlined in the foregoing in-depth study of "Carbon Black Manufacture by the Furnace Process" there are four continuous and two intermittent vent streams to the atmosphere.

1. Continuous Streams

- (a) Main Process Vent Gas - This consists of the gross reactor effluent plus quench water after recovery of carbon black product and represents the primary source of emissions from the plant.
- (b) Product Transport Vent - Some plants incorporate pneumatic conveyors for moving product to the finishing area. The carrier gas for this operation is vented to the atmosphere after recovery of entrained carbon black.
- (c) Drier Vent(s) - In most plants a major portion of the hot gas employed in the product drying operation does not come in contact with carbon black but is used as an indirect heat source and, therefore, contains no entrained carbon black. The only consequence of this stream, with respect to atmosphered contaminants, is due to the products of combustion from natural gas. The remaining portion of the hot gas used in drying and representing 35 to 70% of the total is charged directly to the drier interior for removal of water vapor. This latter stream will contain carbon particles and is vented after passing through a filter or water scrubber for particulate removal.

- (d) **Bagging and Storage Area Vent** - Carbon black content of this air stream varies depending upon specific operations being performed in the storage area. The emissions from this source could be significantly reduced temporarily without a loss in production by curtailing the bagging operation if adequate bulk storage is available.

2. Intermittent Air Emissions

- (a) **Vacuum Clean-Up** - The vacuum clean-up system is usually in a standby condition with carbon black only present in the exhaust stream when the system is being used to clean-up carbon spills. However, in some plants bagging and storage areas are an adjunct of the clean-up system. In this case, some emissions would always be present if the plant was in operation.
- (b) **Emergency Relief** - It is assumed that this consists of vent gas from pressure safety valves or expansion discs and would occur very infrequently.

C. Abatement Techniques

As the various levels of the pre-planned episode reduction scheme are declared (Alert, Warning and Emergency) a progressive reduction in emissions of air pollutants must be made. This could ultimately lead to total curtailment of pollutant emissions if the emergency level becomes imminent. The extent of required cutback in emissions from carbon black plants will depend on the relative amount of offending constituents contributed by carbon black production to the overall emissions which resulted in the pollution episode. This plus other factors will be used by control authorities in determining the amount of emissions to be tolerated during various episodes.

Carbon black manufacturing facilities generally consist of several units with each unit being composed of two or more reactors attached to a single collection system. This provides for a certain degree of flexibility for a partial reduction in air pollutant emissions during an air pollution alert. Several options are available to accomplish this reduction:

Option 1 - Ceasing production on one or more reactors of a given unit and then placing these reactors on heating load by maintaining air flow and using natural gas for temperature control.

Option 2 - Ceasing production on one or more entire units and maintaining them on heating load.

Option 3 - A carbon black manufacturing plant has a certain inherent inflexibility with respect to operating conditions, with a delicate balance between operating variables and product quality. However, a turndown of feed rate is possible in some

cases for a partial reduction in emissions. It has been reported that atmospheric emissions from the various vent streams are directly proportional to quantity of carbon black being produced.

Option 4 - If the contaminant producing the air pollution episode is sulfur, the utilization of a lower sulfur content feedstock could produce the desired reduction of pollutant.

In the case of Option 1, the curtailment of operation of one or more reactors of a given unit must be considered with respect to downstream emission. For example, in plants that employ thermal incinerators or plume burners, removal of feed stock from one or more reactors of a unit while maintaining these reactors on heating load would decrease the amount of combustibles flowing to the combustion device. Unless adequate supplemental fuel is available to replace these combustibles, lower incineration temperature or burner flame out could occur resulting in a net increase in emissions from the operating units. An alternate to Option 1 would be to either directly vent standby reactors to the atmosphere or to forego the maintenance of these reactors on heating load. This latter approach would result in an economic hardship since shutdown time would be as much as three hours with several days required to heat up and return these reactors to productive operation. Whereas to place an operating reactor on hot standby operation requires about one hour and to resume productive operation requires another two to three hours.

In the case of Option 2, the same general comments outlined above are applicable with respect to those plants containing combustion devices as a control of emissions. The alternate in Option 2 would be to forego the maintenance of the standby condition and accept the resulting economic hardship.

The overall quantity of emissions produced depend on the type of carbon black being manufactured. Soft black reactors produce approximately one-half the emissions of a hard black producing reactor. Since most plants produce both types of carbon black, the manufacturer has some flexibility in determining which reactors or units are to be shutdown or placed in standby in order to reduce emissions to prescribed levels.

Product recovery bag filters will remain in service during shutdown and startup. Consequently, particulate emissions in the bag filter effluent will not increase under these circumstances. Therefore, the choice in operations outlined in Options 1 and 2 to effect a partial reduction in atmospheric pollutants depends primarily on the facilities that control the pollutants contained in the filter bag effluent. In plants that send the bag filter effluent to an incinerator, the alternates in Option 1 and 2 would be in force. This results in reduced flow to the incinerator and, due to longer residence time, will permit a reduction in furnace operating temperature. This in turn should offset the tendency to form more NO_x caused by the increased residence time. However, if the incinerators include steam generation facilities, it may be necessary to continue operation of this pollution control system at normal levels during the alert utilizing additional supplemental fuel.

Plants employing water scrubbers on the main process vent and/or drier vent streams will continue to run this item at design water rates during an alert. This should improve scrubbing efficiency over that obtained at normal carbon black production levels.

1. Declaration of Alert Condition - When an alert condition is declared, the episode emission reduction plan is immediately set into motion. Under this plan, in addition to notifying the manufacturer of the alert condition, it may be deemed necessary by the Environmental Protection Authorities to reduce emissions from carbon black manufacture by a small amount in order to deter further increases in pollution level which could result in warning or emergency episodes. This may be accomplished by employing one of the foregoing options. The specific option to be used for the reduction is at the discretion of the manufacturer. The time required to affect the reduction will depend on the route selected and will be approximately as stated in the preceding discussion. This will reduce the principal source of emissions, represented by the main process vent, to a value equivalent to the reduction made in the producing units. The other sources of emission, represented by the product transport vent (if pneumatic conveyor), drier vents, bagging and storage vents and the vacuum clean-up vent will be reduced to some degree by virtue of the reduction made in the producing equipment. Usually the alert condition can be expected to continue for 12 hours or more.
2. Declaration of Warning Condition - When the air pollution emergency episode is announced a substantial reduction of air contaminants is desirable even to the point of assuming reasonable economic hardship in the cutback of production and allied operations. This could involve a 50 to 60 percent decrease in carbon black production.
3. Emergency Condition - When it appears that an air pollution emergency episode is imminent, all air contaminants may have to be eliminated immediately by ceasing production and allied operations to the extent possible without causing injury to persons or damage to equipment.

The cessation of operation of the producing units whether wholly or in part will not result in increased emissions. This is also true for startup operations since the principal pollution control devices are in service during both operations.

D. Economic Considerations

The economic impact on carbon black manufacturers of curtailing operations during any of the air pollution episodes is based on the duration and number of episodes in a given period. It is indicated that the normal duration of air pollution episodes is usually one to seven days with meteorology episode potentials as high as 80 per year.¹⁹ The frequency of air pollution episodes in any given area is indicated as being one to four per year. These data do not differentiate between the episode levels. Normally since the alert level does not require a cutback in production, it will not influence plant economics. Therefore, in discussing economic considerations resulting from the air pollution abatement plan, it is only necessary to estimate the frequency and number of warning and emergency episodes. For the economic study, it has been

assumed that three warning and no emergency episodes occur during a typical year. Each warning episode is assumed to require a 50 percent reduction in air contaminants for a period of four days with an additional day allocated to returning the plant to full capacity. This then equates to a complete loss in plant production for about eight and one-half days per year.

The financial impact resulting from this loss in production is shown in Table CB-17. This table contains comparative manufacturing costs for an existing 90 MM lbs./year facility without extensive pollution control (Table CB-11) and for a most feasible new facility of the same capacity (Table CB-13). Economics are shown for each of these plants with and without the financial impact accredited to the air pollution episodes. It should be noted that whereas the proposed cutback in carbon black production for emission control appears small (2.5 percent on a yearly basis), it has a substantial influence on net profit (17.5 percent and 21.0 percent reduction respectively).

E. Summary of Estimated Emissions

In the foregoing a reduction in air pollutant emissions was suggested for the various air pollution levels that may be encountered. This was primarily predicated on existing plants which generally utilize bag filters but do not have the more sophisticated pollution control equipment. Special consideration should be made in the EAP for Air Pollution Episode Avoidance for new and existing plants that employ incineration control equipment on the bag filter effluent. The following presents estimated 1985 air emissions for a typical present day system without incineration and the most feasible new plant with this type of control.

<u>Pollutant</u>	<u>Typical Present System Average Emissions, Tons/Ton</u>	<u>Most Feasible New Plant Average Emissions, Tons/Ton</u>
Hydrocarbons + H ₂ S	0.0513	--
Particulate	0.0027	--
NO _x	0.0023	0.0042
SO _x	0.0085	0.0307
CO	<u>1.2907</u>	<u>--</u>
Total Emissions	1.3555	0.0349

As noted in the above, total emissions for the most feasible new plant has been reduced to one-fortieth of that estimated for the typical present system without incineration. However, emissions of NO_x and SO_x are substantially higher for the plant employing an incinerator.

TABLE CB-17
FINANCIAL IMPACT OF AIR POLLUTION EPISODES
ON MANUFACTURING COSTS
FOR 90 MM LBS./YR. CARBON BLACK FACILITY

Sheet 1 of 2

Type of Operation	TYPICAL EXISTING PLANT (a)		MOST FEASIBLE NEW PLANT (b)	
	No Cutback In Production (Table CB-11)	Assuming 8.5 Days Lost Production	No Cutback In Production (Table CB-13)	Assuming 8.5 Days Lost Production
<u>Direct Manufacturing Cost, \$/Yr.</u>				
Feedstock				
Natural Gas @ 40¢/MM BTU	378,000	369,000	378,000	369,000
Oil @ 8.0¢/Gal.	1,287,000	1,255,000	1,287,000	1,255,000
Labor	396,000	396,000	405,000	405,000
Maintenance	531,000	531,000	576,000	576,000
Utilities	387,000	377,000	225,000	222,000
	<u>2,979,000</u>	<u>2,928,000</u>	<u>2,871,000</u>	<u>2,827,000</u>
<u>Indirect Manufacturing Cost, \$/Yr.</u>				
Plant Overhead and Laboratory	648,000	648,000	666,000	666,000
<u>Fixed Manufacturing Cost, \$/Yr.</u>				
Depreciation, Insurance and Property Taxes	1,314,000	1,314,000	1,431,000	1,431,000
<u>Total Manufacturing Cost, \$/Yr.</u>	<u>4,941,000</u>	<u>4,890,000</u>	<u>4,968,000</u>	<u>4,924,000</u>

TABLE CB-17

CONTINUED - PAGE 2

Sheet 2 of 2

Type of Operation	TYPICAL EXISTING PLANT (a)		MOST FEASIBLE NEW PLANT (b)	
	No Cutback In Production (Table CB-11)	Assuming 8.5 Days Lost Production	No Cutback In Production (Table CB-13)	Assuming 8.5 Days Lost Production
General Expenses, \$/Yr.				
Administration, Sales, Research and Finance	945,000	945,000	999,000	999,000
Total Cost, \$/Yr.	5,886,000	5,835,000	5,967,000	5,923,000
Sales, \$/Yr.	6,525,000	6,362,000	6,525,000	6,362,000
Profit Before Taxes	639,000	527,000	558,000	439,000
Profit After 52% Tax	306,700	253,000	267,000	211,000
Cash Flow	1,377,700	1,324,000	1,428,000	1,372,000
ROI (NPAT X 100/Investment)	2.86%	2.36%	2.30%	1.82%

CB-95

- (a) Incorporates bag filters on main process and product handling vent streams, water scrubber on drier purge gas and a vacuum clean-up system.
- (b) Includes thermal incinerator plus waste heat boiler on the effluent from the main process vent gas bag filters. Bag filters are also provided on product handling, drier purge gas and product storage area vent streams.

The particular type and concentration of pollutants in the atmosphere at the time of the episode would dictate the degree to which a reduction would be made on the most feasible new plant. If NO_x and/or SO_x are the offending material, then a reduction in plant production should be made as outlined under "Abatement Techniques". In this case, SO_x emissions would be reduced in direct proportion to the reduction of carbon black production. The NO_x emissions would probably be reduced by a greater percentage because of reduced furnace operating temperature.

If the offending pollutants are in the form of hydrocarbons, particulate or CO, less severe cutbacks in production need to be taken on the declaration of warning condition.

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APPENDIX I

BASIS OF THE STUDY

I. Industry Survey

The study which led to this document was undertaken to obtain information about selected production processes that are practiced in the Petrochemical Industry. The objective of the study was to provide data for the EPA to use in the fulfillment of their obligations under the Clean Air Amendments of 1970.

The information obtained during the study includes industry descriptions, air emission control problems, sources of air emissions, statistics on quantities and types of emissions and descriptions of emission control devices currently in use. The principal source for these data was an Industry Questionnaire but it was supplemented by plant visits, literature searches, in-house background knowledge and direct support from the Manufacturing Chemists Association.

More than 200 petrochemicals are currently produced in the United States, and many of these by two or more different processes. It was obvious that the most immediate need was to study the largest tonnage, fastest growth processes that produce the most pollution. Consequently, the following 32 chemicals (as produced by a total of 41 different processes) were selected for study:

Acetaldehyde (two processes)	Nylon 6
Acetic Acid (three processes)	Nylon 6,6
Acetic Anhydride	"Oxo" Alcohols and Aldehydes
Acrylonitrile	Phenol
Adipic Acid	Phthalic Anhydride (two processes)
Adiponitrile (two processes)	Polyethylene (high density)
Carbon Black	Polyethylene (low density)
Carbon Disulfide	Polypropylene
Cyclohexanone	Polystyrene
Ethylene	Polyvinyl Chloride
Ethylene Dichloride (two processes)	Styrene
Ethylene Oxide (two processes)	Styrene - Butadiene Rubber
Formaldehyde (two processes)	Terephthalic Acid (1)
Glycerol	Toluene Di-isocyanate (2)
Hydrogen Cyanide	Vinyl Acetate (two processes)
Maleic Anhydride	Vinyl Chloride

(1) Includes dimethyl terephthalate.

(2) Includes methylenediphenyl and polymethylene polyphenyl isocyanates.

The Industry Questionnaire, which was used as the main source of information, was the result of cooperative efforts between the EPA, Air Products and the EPA's Industry Advisory Committee. After receiving approval from the Office of Management and Budget, the questionnaire was sent to selected producers of most of the chemicals listed above. The data obtained from the returned questionnaires formed the basis for what have been named "Survey Reports". These have been separately published in four volumes, numbered EPA-450/3-73-005a, b, c, and d and entitled "Survey Reports on Atmospheric Emissions from the Petrochemical Industry - Volumes I, II, III, and IV.

The purpose of the survey reports was to screen the various petrochemical processes into the "more" and "less - significantly polluting processes". Obviously, significance of pollution is a term which is difficult if not impossible to define because value judgements are involved. Recognizing this difficulty, a quantitative method for Significant Emission Index (SEI) was developed. This procedure is discussed and illustrated in Appendix II of this report. Each survey report includes the calculation of an SEI for the petrochemical that is the subject of the report. These SEI's have been incorporated into the Emission Summary Table that constitutes part of this Appendix (Table I). This table can be used as an aid when establishing priorities in the work required to set standards for emission controls on new stationary sources of air pollution in accordance with the terms of the Clean Air Amendments of 1970.

The completed survey reports constitute a preliminary data bank on each of the processes studied. In addition to the SEI calculation, each report includes a general introductory discussion of the process, a process description (including chemical reactions), a simplified process flow diagram, as well as heat and material balances. More pertinent to the air pollution study, each report lists and discusses the sources of air emissions (including odors and fugitive emissions) and the types of air pollution control equipment employed. In tabular form, each reports summarizes the emission data (amount, composition, temperature, and frequency); the sampling and analytical techniques; stack numbers and dimensions; and emission control device data (types, sizes, capital and operating costs, and efficiencies).

Calculation of efficiency on a pollution control device is not necessarily a simple and straight-forward procedure. Consequently, two rating techniques were developed for each type of device, as follows:

1. For flares, incinerators, and boilers a Completeness of Combustion Rating (CCR) and Significance of Emission Reduction Rating (SERR) were used.
2. For scrubbers and dust removal equipment, a Specific Pollutant Efficiency (SE) and a SERR were used.

The bases for these ratings and example calculations are included in Appendix III of this report.

II. In-Depth Studies

The original performance concept was to select a number of petrochemical processes as "significant polluters", on the basis of data contained in completed questionnaires. These processes were then to be studied "in-depth". However, the overall time schedule was such that the EPA requested an initial selection of three processes on the basis that they would probably turn out to be "significant polluters". The processes selected in this manner were:

1. The Furnace Process for producing Carbon Black.
2. The Sohio Process for producing Acrylonitrile.
3. The Oxychlorination Process for producing 1,2 Dichloroethane (Ethylene Dichloride) from Ethylene.

TABLE I
EMISSIONS SUMMARY

Page 1 of 3

	ESTIMATED (1) CURRENT AIR EMISSIONS, MM LBS./YEAR					
	Hydrocarbons (3)	Particulates (4)	Oxides of Nitrogen	Sulfur Oxides	Carbon Monoxide	Total Weighted (5)
Acetaldehyde via Ethylene via Ethanol	1.1	0	0	0	0	86
Acetic Acid via Methanol	0	0	0	0	27	27
via Butene	40	0	0.01	0	0.01	1
via Acetaldehyde	6.1	0	0.04	0	54	3,215
Acetic Anhydride via Acetic Acid	3.1	0	0	0	14	490
Acrylonitrile (9)	183	0	0	0	1.3	253
Adipic Acid	0	0.2	5.5	0	5.5	15,000
Adiponitrile via Butadiene	11.2	4.7	29.6	0	196	1,190
via Adipic Acid	0	0.5	50.5	0	0.14	3,200
Carbon Black	156	8.1	0.04	0	0	30
Carbon Disulfide	0.15	0.3	6.9	21.6	3,870	17,544
Cyclohexanone	70	0	0.1	4.5	0	120
Dimethyl Terephthalate (MTPA)	91	1.4	0.1	1.0	77.5	5,700
Ethylene	15	0.2	0.2	2.0	53	7,460
Ethylene Dichloride via Oxichlorination	95.1	0.4	0	0	0.2	1,240
via Direct Chlorination	29	0	0	0	21.8	7,650
Ethylene Oxide	85.8	0	0.3	0.1	0	2,300
Formaldehyde via Silver Catalyst	23.8	0	0	0	0	6,880
via Iron Oxide Catalyst	25.7	0	0	0	107.2	1,955
Glycerol via Epichlorohydrin	16	0	0	0	24.9	2,070
Hydrogen Cyanide Direct Process	0.5	0	0.41	0	0	16
Isocyanates	1.3	0.8	0	0.02	86	56
Maleic Anhydride	34	0	0	0	260	231
Nylon 6	0	1.5	0	0	0	90
Nylon 6,6	0	5.5	0	0	0	330
Oxo Process	5.25	0.01	0.07	0	19.5	440
Phenol	24.3	0	0	0	24.3	1,940
Phthalic Anhydride via O-Xylene	0.1	5.1	0.3	2.6	43.6	422
via Naphthalene	0	1.9	0	0	45	160
High Density Polyethylene	79	2.3	0	0	0	6,400
Low Density Polyethylene	75	1.4	0	0	0	6,100
Polypropylene	37.5	0.1	0	0	0	2,950
Polystyrene	20	0.4	0	1.2	0	1,650
Polyvinyl Chloride	62	12	0	0	0	5,700
Styrene	4.3	0.07	0.14	0	74	355
Styrene-Butadiene Rubber	9.4	1.6	0	0.9	4.5	870
Vinyl Acetate via Acetylene	5.3	0	0	0	0	425
via Ethylene	0	0	TR	0	TR	TR
Vinyl Chloride	17.6	0.6	0	0	18.2	1,460
Totals	1,227.6	49.1	94.2	33.9	4,852.6	110,220 (7)

- (1) In most instances numbers are based on less than 100% survey. All based on engineering judgement of best current control. Probably has up to 10% low bias.
- (2) Annemex future plants will employ best current control techniques.
- (3) Excludes methane, includes H₂ and all volatile organics.
- (4) Includes non-volatile organics and inorganics.
- (5) Weighting factors used are: hydrocarbons - 80, NO_x - 40, SO_x - 20, and CO - 1.
- (6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
- (7) Totals are not equal across and down due to rounding.
- (8) Emissions based on what is now an obsolete catalyst. See Report No. EPA-450/3-73-006 b for up-to-date information.

TABLE I
EMISSION SUMMARY

Page 2 of 3

ESTIMATED ADDITIONAL (2) AIR EMISSIONS IN 1980, MM LBS./YEAR

	Hydrocarbons (3)	Particulates (4)	Oxides of Nitrogen	Sulfur Oxides	Carbon Monoxide	Total	Total Weighted (5,6)
Acetaldehyde via Ethylene via Ethanol	1.2	0	0	0	0	1.2	96
Acetic Acid via Methanol via Butane	0	0	0	0	0	0	0
Acetic Anhydride via Acetic Acid	0	0	0.04	0	0	0.04	2
Acrylonitrile (9)	12.2	0	0	0	0	14.7	980
Adipic Acid	0.73	0	0	0	2.5	2.15	60
Adiponitrile via Butadiene via Adipic Acid	284	0	8.5	0	304	596	23,000
Carbon Black	0	0.14	19.3	0	0.09	19.5	779
Carbon Monoxide	10.5	4.4	47.5	0	0	62.4	3,010
Cyclohexanone	64	0.5	0.04	0	0	0.54	30
Dimethyl Terephthalate (+TPA)	77.2	3.3	2.8	8.9	1,590	1,670	7,200
Ethylene Dichloride via Oxichlorination via Direct Chlorination	0.04	0.07	0.03	1.1	0	1.24	30
Ethylene Oxide	73.8	1.1	0.07	0.84	85.1	162	6,260
Formaldehyde via Silver Catalyst	14.8	0.2	0.2	61.5	42.9	118.7	6,040
Glycerol via Epichlorohydrin	17.6	0.5	0	0	25	77	2,430
Hydrogen Cyanide Direct Process	8.9	0	0	0	0	136	8,800
Isocyanates	0	0	0	0	0	34.2	2,740
Maleic Anhydride	1.2	0.7	0	0.02	85	87	225
Nylon 6	31	3.2	0	0	241	272	2,720
Nylon 6,6	0	5.3	0	0	0	3.2	194
One Process	3.86	0.01	0.05	0	14.3	18.2	318
Phenol	21.3	0	0	0	0	21.3	325
Phthalic Anhydride via O-Xylene via Naphthalene	0.3	13.2	0.8	6.8	113	134	1,704
High Density Polyethylene	210	6.2	0	0	0	0	1,100
Low Density Polyethylene	262	5	0	0	0	216	17,200
Polypropylene	152	0.5	0	0	0	267	21,300
Polystyrene	20	0.34	0	1.13	0	132.5	12,190
Polyvinyl Chloride	53	10	0	0	0	21.47	1,640
Styrene	3.1	0.05	0.1	0	0	63	4,840
Styrene-Butadiene Rubber	1.85	0.31	0	0.18	0	3.25	225
Vinyl Acetate via Acetylene via Ethylene	4.5	0	0	0	0	2.34	170
Vinyl Chloride	0	0	TR	0	0	4.5	360
	26.3	0.2	0	0	0	TR	TR
Totals	1,547.2	55.9	79.5	80.5	2,588	27.2	2,170
							134,213 (7)

(1) In most instances numbers are based on less than 100% survey. All based on engineering judgement of best current control. Probably has up to 10% low bias.

(2) Assumes future plants will employ best current control techniques.

(3) Excludes methanol, includes H₂S and all volatile organics.

(4) Includes non-volatile organics and inorganics.

(5) Weighting factors used are: hydrocarbons - 80, particulates - 60, NO_x - 40, SO_x - 40, and CO - 1.

(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".

(7) Totals are not equal across and down due to rounding.

(8) See sheet 1 of 3.

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TABLE I
EMISSIONS SUMMARY

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	Emissions (2), MM Lbs./Year		Estimated Number of New Plants (1973 - 1980)	Total Estimated Capacity MM Lbs./Year	
	Total by 1980	Total Weighted (5) by 1980		Current	By 1980
Acetaldehyde via Ethylene	2.3	182	6	1,160	2,460
via Ethanol	27	27	0	966	966
Acetic Acid via Methanol	0.05	3	4	400	1,800
via Butane	54	3,215	0	1,020	500
via Acetaldehyde	22	1,470	3	875	2,015
Acetic Anhydride via Acetic Acid	10.8	313	3	1,705	2,100
Acrylonitrile (9)	980	38,000	5	1,165	3,700 (8)
Adipic Acid	50	1,970	7	1,430	2,200
Adiponitrile via Butadiene	128.8	6,210	4	435	865
via Adipic Acid	1.1	60	3	280	550
Carbon Black	5,730	24,740	13	3,000	5,000 (8)
Carbon Disulfide	6.3	150	2	871	1,100
Cyclohexanone	310	11,960	10	1,800	3,600
Dimethyl Terephthalate (+TPA)	265	13,500	8	2,865	5,900
Ethylene	94	3,670	21	22,295	40,000
Ethylene Dichloride via Oxychlorination	253	16,450	8	4,450	8,250 (8)
via Direct Chlorination	63	5,040	10	5,593	11,540
Ethylene Oxide	120	9,530	15	4,191	6,800 (8)
Formaldehyde via Silver Catalyst	212.5	3,205	40	5,914	9,000
via Iron Oxide Catalyst	85	3,515	12	1,729	3,520 (8)
Glycerol via Epichlorohydrin	25	2,000	1	245	380
Hydrogen Cyanide Direct Process	0.5 (10)	28 (10)	0	412	202
Isocyanates	175	456	10	1,088	2,120
Maleic Anhydride	566	5,670	6	359	720
Nylon 6	4.7	284	10	486	1,500
Nylon 6,6	10.8	650	10	1,523	3,000
Oxo Process	43	765	6	1,727	3,000
Phenol	46	3,640	11	2,363	4,200
Phthalic Anhydride via O-Xylene	186	1,522	6	720	1,800 (8)
via Naphthalene	47	160	0	603	528
High Density Polyethylene	297	23,600	31	2,315	8,500
Low Density Polyethylene	343	27,400	41	5,269	21,100
Polypropylene	190	15,140	32	1,160	5,800
Polystyrene	43	3,290	23	3,500	6,700
Polyvinyl Chloride	137	10,540	25	4,375	8,000
Styrene	7.4	610	9	5,953	10,000
Styrene-Butadiene Rubber	14	1,040	4	4,464	5,230
Vinyl Acetate via Acetylene	9.8	785	1	206	356
via Ethylene	TR	TR	4	1,280	2,200
Vinyl Chloride	45	3,630	10	5,400	13,000
Totals	10,605 (7)	244,420 (7)			

(1) In most instances numbers are based on less than 100% survey. All based on engineering judgement of best current control. Probably has up to 10% low bias.

(2) Assumes future plants will employ best current control techniques.

(3) Excludes methane, includes H₂S and all volatile organics.

(4) Includes non-volatile organics and inorganics.

(5) Weighting factors used are: hydrocarbons - 80, particulates - 60, NO_x - 40, SO_x - 20, and CO - 1.

(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".

(7) Totals are not equal across and down due to rounding.

(8) By 1985.

(9) See sheet 1 of 3

(10) Due to anticipated future shut down of marginal plants.

In order to obtain data on these processes, the operators and/or licensors of each were approached directly by Air Products' personnel. This, of course, was a slow and tedious method of data collection because mass mailing techniques could not be used, nor could the request for data be identified as an "Official EPA Requirement". Yet, by the time that OMB approval was given for use of the Industry Questionnaire, a substantial volume of data pertaining to each process had already been received. The value of this procedure is indicated by the fact that first drafts of these three reports had already been submitted to the EPA, and reviewed by the Industry Advisory Committee, prior to the completion of many of the survey reports.

In addition, because of timing requirements, the EPA decided that three additional chemicals be "nominated" for in-depth study. These were phthalic anhydride, formaldehyde and ethylene oxide. Consequently, four additional in-depth studies were undertaken, as follows:

1. Air Oxidation of Ortho-Xylene to produce Phthalic Anhydride.
2. Air Oxidation of Methanol in a Methanol Rich Process to produce Formaldehyde over a Silver Catalyst. (Also, the subject of a survey report.)
3. Air Oxidation of Methanol in a Methanol-Lean Process to produce Formaldehyde over an Iron Oxide Catalyst.
4. Direct Oxidation of Ethylene to produce Ethylene Oxide.

The primary data source for these was the Industry Questionnaire, although SEI rankings had not been completed by the time the choices were made.

The Survey Reports, having now been completed are available, for use in the selection of additional processes for in-depth study.

INTRODUCTION TO APPENDIX II AND III

The following discussions describe techniques that were developed for the single purpose of providing a portion of the guidance required in the selection of processes for in-depth study. It is believed that the underlying concepts of these techniques are sound. However, use of them without substantial further refinement is discouraged because the data base for their specifics is not sufficiently accurate for wide application. The subjects covered in the Appendix II discussion are:

1. Prediction of numbers of new plants.
2. Prediction of emissions from the new plants on a weighted (significance) basis.

The subject covered in the Appendix III discussion is:

Calculation of pollution control device efficiency on a variety of bases, including a weighted (significance) basis.

It should be noted that the weighting factors used are arbitrary. Hence, if any reader of this report wishes to determine the effect of different weighing factors, the calculation technique permits changes in these, at the reader's discretion.

APPENDIX IINumber of New Plants*

Attached Table 1 illustrates the format for this calculation. Briefly, the procedure is as follows:

1. For each petrochemical that is to be evaluated, estimate what amount of today's production capacity is likely to be on-stream in 1980. This will be done by subtracting plants having marginal economics due either to their size or to the employment of an out-of-date process.
2. Estimate the 1980 demand for the chemical and assume a 1980 installed capacity that will be required in order to satisfy this demand.
3. Estimate the portion of the excess of the 1980 required capacity over today's remaining capacity that will be made up by installation of each process that is being evaluated.
4. Estimate an economic plant or unit size on the basis of today's technology.
5. Divide the total required new capacity for each process by the economic plant size to obtain the number of new units.

In order to illustrate the procedure, data have been incorporated into Table I, for the three processes for producing carbon black, namely the furnace process, the relatively non-polluting thermal process, and the non-growth channel process.

*The format is based on 1980, but any future year may be selected.

Table 1. Number of New Plants by 1980

<u>Chemical</u>	<u>Process</u>	<u>Current Capacity</u>	<u>Marginal Capacity</u>	<u>Current Capacity on-stream in 1980</u>	<u>Demand 1980</u>	<u>Capacity 1980</u>	<u>Capacity to be Added</u>	<u>Economic Plant Size</u>	<u>Number of New Units</u>
Carbon Black	Furnace	4,000	0	4,000	4,500	5,000	1,000	90	11 - 12
	Channel	100	0	100	100	100	0	30	0
	Thermal	200	0	200	400	500	300	150	2

II-2

Notes: 1. Capacity units all in MM lbs./year.

2. 1980 demand based on studies prepared for EPA by Processes Research, Inc. and MSA Research Corporation.

Increased Emissions (Weighted) by 1980

Attached Table 2 illustrates the format for this calculation. However, more important than format is a proposal for a weighting basis. There is a wide divergence of opinion on which pollutants are more noxious and even when agreement can be reached on an order of noxiousness, disagreements remain as to relative magnitudes for tolerance factors. In general pollutants from the petrochemical industry can be broken down into categories of hydrogen sulfide, hydrocarbons, particulates, carbon monoxide, and oxides of sulfur and nitrogen. Of course, two of these can be further broken down; hydrocarbons into paraffins, olefins, chlorinated hydrocarbons, nitrogen or sulfur bearing hydrocarbons, etc. and particulates into ash, catalyst, finely divided end products, etc. It was felt that no useful end is served by creating a large number of sub-groupings because it would merely compound the problem of assigning a weighting factor. Therefore, it was proposed to classify all pollutants into one of five of the six categories with hydrogen sulfide included with hydrocarbons.

There appears to be general agreement among the experts that carbon monoxide is the least noxious of the five and that NO_x is somewhat more noxious than SO_x . However, there are widely divergent opinions concerning hydrocarbons and particulates - probably due to the fact that these are both widely divergent categories. In recent years, at least two authors have attempted to assign tolerance factors to these five categories. Babcock (1), based his on the proposed 1969 California standards for one hour ambient air conditions with his own standard used for hydrocarbons.

On the other hand, Walther (2), based his ranking on both primary and secondary standards for a 24-hour period. Both authors found it necessary to extrapolate some of the basic standards to the chosen time period. Their rankings, on an effect factor basis with carbon monoxide arbitrarily used as a reference are as follows:

<u>Babcock</u>		<u>Walther</u>	
		<u>Primary</u>	<u>Secondary</u>
Hydrocarbons	2.1	125	125
Particulates	107	21.5	37.3
NO_x	77.9	22.4	22.4
SO_x	28.1	15.3	21.5
CO	1	1	1

Recognizing that it is completely unscientific and potentially subject to substantial criticism it was proposed to take arithmetic averages of the above values and round them to the nearest multiple of ten to establish a rating basis as follows:

	<u>Average</u>	<u>Rounded</u>
Hydrocarbons	84.0	80
Particulates	55.3	60
NO_x	40.9	40
SO_x	21.6	20
CO	1	1

Table 2. Weighted Emission Rates

Chemical				
Process				
Increased Capacity				
Pollutant	Emissions, Lbs./Lb.	Increased Emissions Lbs./Year	Weighting Factors	Weighted Emissions Lbs./Year
Hydrocarbons			80	
Particulates			60	
NO _x			40	
SO _x			20	
CO			1	
Total				

Increased Emissions (Weighted) by 1980 (continued)

This ranking can be defended qualitatively, if not quantitatively for the following reasons:

1. The level of noxiousness follows the same sequence as is obtained using national air quality standards.
2. Approximately two orders of magnitude exist between top and bottom rankings.
3. Hydrocarbons should probably have a lower value than in the Walther analysis because such relatively non-noxious compounds as ethane and propane are included.
4. Hydrocarbons should probably have a higher value than in the Babcock analysis because such noxious (or posionous) substances as aromatics, chlorinated hydrocarbons, phenol, formaldehyde, and cyanides are included.
5. Particulates should probably have a higher value than in the Walther analysis because national air standards are based mostly on fly ash while emissions from the petrochemical industry are more noxious being such things as carbon black, phthalic anhydride, PVC dust, active catalysts, etc.
6. NO_x should probably have a higher value than in the Walther analysis because its role in oxidant synthesis has been neglected. This is demonstrated in Babcock's analysis.

Briefly, the procedure, using the recommended factors and Table 2, is as follows:

1. Determine the emission rate for each major pollutant category in terms of pounds of pollutant per pound of final product. (This determination was made, on the basis of data reported on returned questionnaires, in the Survey Reports).
2. Multiply these emission rates by the estimate of increased production capacity to be installed by 1980 (as calculated while determining the number of new plants), to determine the estimated pounds of new emissions of each pollutant.
3. Multiply the pounds of new emissions of each pollutant by its weighting factor to determine a weighted pounds of new emissions for each pollutant.
4. Total the weighted pounds of new emissions for all pollutants to obtain an estimate of the significance of emission from the process being evaluated. It was proposed that this total be named "Significant Emission Index" and abbreviated "SEI".

It should be pointed out that the concepts outlined above are not completely original and considerable credit should be given to Mr. L. B. Evans of the EPA for setting up the formats of these evaluating procedures.

Increased Emissions (Weighted) by 1980 (continued)

- (1) Babcock, L. F., "A Combined Pollution Index for Measurement of Total Air Pollution," JAPCA, October, 1970; Vol. 20, No. 10; pp 653-659
- (2) Walther, E. G., "A Rating of the Major Air Pollutants and Their Sources by Effect", JAPCA, May, 1972; Vol. 22, No. 5; pp 352-355

Appendix III
Efficiency of Pollution Control Devices

Incinerators and Flares

The burning process is unique among the various techniques for reducing air pollution in that it does not remove the noxious substance but changes it to a different and hopefully less noxious form. It can be, and usually is, a very efficient process when applied to hydrocarbons, because when burned completely the only products of combustion are carbon dioxide and water. However, if the combustion is incomplete a wide range of additional products such as cracked hydrocarbons, soot and carbon monoxide might be formed. The problem is further complicated if the hydrocarbon that is being burned is halogenated, contains sulfur or is mixed with hydrogen sulfide, because hydrogen chloride and/or sulfur oxides then become products of combustion. In addition, if nitrogen is present, either as air or nitrogenated hydrocarbons, oxides of nitrogen might be formed, depending upon flame temperature and residence time.

Consequently, the definition of efficiency of a burner, as a pollution control device, is difficult. The usual definition of percentage removal of the noxious substance in the feed to the device is inappropriate, because with this definition, a "smoky" flare would achieve the same nearly 100 percent rating, as a "smokeless" one because most of the feed hydrocarbon will have either cracked or burned in the flame. On the other hand, any system that rates efficiency by considering only the total quantity of pollutant in both the feed to and the effluent from the device would be meaningless. For example, the complete combustion of one pound of hydrogen sulfide results in the production of nearly two pounds of sulfur dioxide, or the incomplete combustion of one pound of ethane could result in the production of nearly two pounds of carbon monoxide.

For these reasons, it was proposed that two separate efficiency rating be applied to incineration devices. The first of these is a "Completeness of Combustion Rating" and the other is a "Significance of Emission Reduction Rating", as follows:

1. Completeness of Combustion Rating (CCR)

This rating is based on oxygen rather than on pollutants and is the pounds of oxygen that react with the pollutants in the feed to the device, divided by the theoretical maximum number of pounds that would react: Thus a smokeless flare would receive a 100 percent rating while a smoky one would be rated somewhat less, depending upon how incomplete the combustion.

In utilizing this rating, it is clear that carbon dioxide and water are the products of complete combustion of hydrocarbons. However, some question could occur as to the theoretical completion of combustion when burning materials other than hydrocarbons. It was recommended that the formation of HX be considered complete combustion of halogenated hydrocarbons since the oxidation most typically does not change the valence of the halogen. On the other hand, since some incinerators will be catalytic in nature it was recommended that sulfur trioxide be considered as complete oxidation of sulfur bearing compounds.

Efficiency of Pollution Control Devices

1. Completeness of Combustion Rating (CCR) (continued)

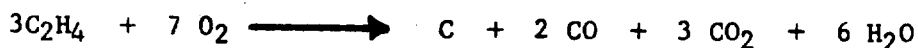
Nitrogen is more complex, because of the equilibria that exist between oxygen, nitrogen, nitric oxide, nitrogen dioxide and the various nitrogen radicals such as nitrile. In fact, many scientists continue to dispute the role of fuel nitrogen versus ambient nitrogen in the production of NO_x . In order to make the CCR a meaningful rating for the incineration of nitrogenous wastes it was recommended that complete combustion be defined as the production of N_2 , thus assuming that all NO_x formed comes from the air rather than the fuel, and that no oxygen is consumed by the nitrogen in the waste material. Hence, the CCR becomes a measure of how completely the hydrocarbon content is burned, while any NO_x produced (regardless of its source) will be rated by the SERR as described below.

2. Significance of Emission Reduction Rating (SERR)

This rating is based primarily on the weighting factors that were proposed above. All air pollutants in the feed to the device and all in the effluents from the device are multiplied by the appropriate factor. The total weighted pollutants in and out are then used in the conventional manner of calculating efficiency of pollutant removal, that is pollutants in minus pollutants out, divided by pollutants in, gives the efficiency of removal on a significance of emission basis.

Several examples will serve to illustrate these rating factors. as follows:

Example 1 - One hundred pounds of ethylene per unit time is burned in a flare, in accordance with the following reaction:



Thus, 14.2 lbs. of particulate carbon and 66.5 lbs. of carbon monoxide are emitted, and 265 lbs. of oxygen are consumed.

Theoretical complete combustion would consume 342 lbs. of oxygen in accordance with the following reaction:



Thus, this device would have a CCR of $265/342$ or 77.5%.

Assuming that one pound of nitric oxide is formed in the reaction as a result of the air used for combustion (this is about equivalent to 100 ppm), a SERR can also be calculated. It should be noted that the formation of this NO is not considered in calculating a CCR because it came from nitrogen in the air rather than nitrogen in the pollutant being incinerated. The calculation follows:

Efficiency of Pollution Control Devices2. Significance of Emission Reduction Rating (SERR) (continued)

<u>Pollutant</u>	<u>Weighting Factor</u>	<u>Pounds in</u>		<u>Pounds out</u>	
		<u>Actual</u>	<u>Weighted</u>	<u>Actual</u>	<u>Weighted</u>
Hydrocarbons	80	100	8000	0	
Particulates	60	0		14.2	852
NO _x	40	0		1	40
SO _x	20	0		0	
CO	1	0	—	66.5	66.5
Total			8000		958.5

$$\text{SERR} = \frac{8000 - 958.5}{8000} \times 100 = 88\%$$

Example 2 - The same as Example 1, except the hydrocarbons are burned to completion. Then,

$$\text{CCR} = \frac{342}{342} \times 100 = 100\%$$

and

$$\text{SERR} = \frac{8000 - 40}{8000} = 99.5\%$$

Example 3 - One hundred pounds per unit time of methyl chloride is incinerated, in accordance with the following reaction.



This is complete combustion, by definition, therefore, the CCR is 100%. However, (assuming no oxides of nitrogen are formed), the SERR is less than 100% because 72.5 lbs. of HCl are formed. Hence, considering HCl as an aerosol or particulate;

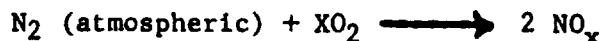
$$\text{SERR} = \frac{100 \times 80 - 72.5 \times 60}{100 \times 80} \times 100 = 45.5\%$$

The conclusion from this final example, of course, is that it is an excellent combustion device but a very poor pollution control device, unless it is followed by an efficient scrubber for HCl removal.

Example 4 - The stacks of two hydrogen cyanide incinerators, each burning 100 pounds per unit time of HCN are sampled. Neither has any carbon monoxide or particulate in the effluent. However, the first is producing one pound of NO_x and the second is producing ten pounds of NO_x in the same unit time. The assumed reactions are:

Efficiency of Pollution Control Devices

2. Significance of Emission Reduction Rating (SERR) (continued)



Thus, $\text{CCR}_1 = 100\%$ and $\text{CCR}_2 = 100\%$ both by definition.

$$\text{However, } \text{SERR}_1 = \frac{100 \times 80 - 1 \times 40}{100 \times 80} \times 100 = 99.5\%$$

$$\text{and } \text{SERR}_2 = \frac{100 \times 80 - 10 \times 40}{100 \times 80} \times 100 = 95\%$$

Obviously, if either of these were "smoky" then both the CCR and the SERR would be lower, as in Example 1.

Other Pollution Control Devices

Most pollution control devices, such as bag filters, electrostatic precipitators and scrubbers are designed to physically remove one or more noxious substances from the stream being vented. Typically, the efficiency of these devices is rated relative only to the substance which they are designed to remove and for this reason could be misleading. For example:

1. The electrostatic precipitator on a power house stack might be 99% efficient relative to particulates, but will remove little or none of the SO_x and NO_x which are usually present.
2. A bag filter on a carbon black plant will remove 99 + % of the particulate but will remove none of the CO and only relatively small amounts of the compounds of sulfur that are present.
3. A water scrubber on a vinyl chloride monomer plant will remove all of the hydrogen chloride but only relatively small amounts of the chlorinated hydrocarbons present.
4. An organic liquid scrubber on an ethylene dichloride plant will remove nearly all of the EDC but will introduce another pollutant into the air due to its own vapor pressure.

For these reasons, it was suggested again that two efficiency ratings be applied. However, in this case, the first is merely a specific efficiency as is typically reported, i.e., "specific to the pollutant (or pollutants) for which it was designed", thus:

$$\text{SE} = \frac{\text{specific pollutant in} - \text{specific pollutant out}}{\text{specific pollutant in}} \times 100$$

The second rating proposed is an SERR, defined exactly as in the case of incinerators.

Two examples will illustrate these ratings.

Efficiency of Pollution Control DevicesOther Pollution Control Devices (continued)

Example 1 - Assume that a catalytic cracker regenerator effluent contains 100 pounds of catalyst dust, 200 lbs. of carbon monoxide and 10 pounds of sulfur oxides per unit time. It is passed through a cyclone separator where 95 pounds of catalyst are removed. Therefore,

$$SE = \frac{100 - 5}{100} \times 100 = 95\%$$

$$\begin{aligned} \text{and SERR} &= \frac{(100 \times 60 + 10 \times 20 + 200 \times 1) - (5 \times 60 + 10 \times 20 + 200 \times 1)}{(100 \times 60 + 10 \times 20 + 200 \times 1)} \times 100 \\ &= \frac{6400 - 700}{6400} \times 100 = 89\% \end{aligned}$$

Example 2 - Assume that an organic liquid scrubber is used to wash a stream containing 50 pounds of SO_2 per unit time. All but one pound of the SO_2 is removed but two pounds of the hydrocarbon evaporate into the vented stream. Then

$$SE = \frac{50 - 1}{50} \times 100 = 98\%$$

$$\begin{aligned} \text{and SERR} &= \frac{(50 \times 20) - (1 \times 20 + 2 \times 80)}{(50 \times 20)} \times 100 \\ &= \frac{1000 - 180}{1000} \times 100 = 82\% \end{aligned}$$