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CARBON BLACK
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5.3
Carbon Black

Introduction

Monsanto Research Corporation (MRC) is under contract to the U.S. Environmental Protection Agency (EPA contract 68-02-1874) to provide sufficient information to enable EPA to determine the need to reduce pollution from stationary sources. The contract is one of EPA's on-going programs to ensure that pollution control technology is available to meet the requirements of environmental legislation. During the contract effort, MRC generates detailed emission inventory data on selected air pollution sources. Emission inventory data generated covers criteria pollutants, hazardous air pollutants, and specific chemical species. This paper presents a summary of emission inventory data generated on the above contract for five chemical manufacturing operations: 1) acrylonitrile manufacture via the propylene oxidation process; 2) phthalic anhydride manufacture from ortho xylene and from naphthalene; 3) carbon black manufacture; 4) synthetic ammonia production; and 5) ammonium nitrate production.

Acrylonitrile Manufacture

In the assessment of acrylonitrile manufacture, MRC evaluated the production of acrylonitrile by the catalytic vapor ammoxidation of propylene using the SOHIO process. The six plants producing 8.62×10^5 metric tons per year were found to have sources of air emissions including absorber vents, the incinerator stack, the flare stack, storage tanks, transport loading, deep well ponds, fugitive sources (valves, flanges, etc.). Besides criteria pollutants, 23 chemical substances are emitted from these sources including compounds such as propylene, propane, acrylonitrile, acetonitrile, hydrogen cyanide, benzene, and toluene.

The major source of uncontrolled hydrocarbon and carbon monoxide emissions was found to be the absorber vent which emitted 87.3% and 99%, respectively, of the total hydrocarbon and CO emissions from the acrylonitrile manufacture.

Emission inventory data were supplied by all manufacturing plants and verified by MRC through field sampling conducted at 2 of the 6 plants. Field sampling was performed on the absorber vent, incinerator stack and deep well pond. Results indicate fairly good agreement (about ±50%) between the fielding sampling data and emissions inventory data supplied by the plants. Table I presents the detailed uncontrolled emission factors for each emission point within acrylonitrile plants while Table II presents the emissions inventory for uncontrolled emissions from all plants. Data in Table II account for 95% control of carbon monoxide and hydrocarbon emissions which is being obtained at 3 plants representing 64% of total production capacity.

Phthalic Anhydride Manufacture

In the assessment of phthalic anhydride manufacture, MRC evaluated the production of phthalic anhydride form ortho-xylene (*o*-xylene) and from naphthalene. *O*-xylene is used as the feedstock at 7 plants representing 67% of total production capacity. Naphthalene is used as the feedstock at 3 plants representing 33% of total production capacity. Total U.S. phthalic anhydride production capacity (excluding Puerto Rico) is 5.05×10^5 metric tons per year. Emission points within phthalic anhydride plants include the main process vent, secondary incinerator, storage tanks, product flaker and

bagger, product transport loading facility, and fugitive emission sources. Criteria and noncriteria pollutants include phthalic anhydride, maleic anhydride, benzoic acid, naphthoquinone, naphthalene, diphenyl oxide, formaldehyde, and *o*-xylene.

The largest source of atmospheric emissions was found to be the main process vent which emits over 99% of the carbon monoxide, 53% of the total hydrocarbons, and most of the chemical species.

Emissions inventory data were supplied by the manufacturing plants and verified by field sampling data available from other sources. Table III presents the detailed uncontrolled and controlled emission factors for *o*-xylene-based and naphthalene-based phthalic anhydride plants. Table IV presents the emission inventory data for all plants as a result of installing emissions controls in the plants.

Carbon Black Manufacture

MRC evaluated the atmospheric emissions from carbon black manufacturing plants which use the oil furnace process and the thermal process. Thirty carbon black plants have a combined production capacity of 1.88×10^6 metric tons per year and typically operate at about 80% of capacity. Emission points within carbon black plants include the main process vent, the dryer vent, the pneumatic system vent, feedstock storage tanks, vacuum clean-up system vent, and fugitive sources. Materials emitted from carbon black plants include the criteria pollutants, two hazardous materials (beryllium and mercury), 14 chemical species, polycyclic organic materials, and trace metals. The major source of uncontrolled emissions was found to be the main process vent.

Emission inventory data were supplied by 15 of the 30 plants. Battelle and MRC performed separate field sampling programs and verified the validity of the emission inventory survey data. Table V presents the detailed uncontrolled emission factors for each emission point in carbon black plants. Table VI presents the 1978 emissions inventory for carbon black plants; it accounts for the fact that 19 of the 30 plants have installed emission control devices obtaining a typical emissions control efficiency of 95% for carbon monoxide and hydrocarbons.

Synthetic Ammonia Manufacture

MRC's evaluated the manufacture of synthetic ammonia of which 98% is produced via the catalytic steam reforming of natural gas. There are 90 plants producing a total of 15.2×10^6 metric tons per year of ammonia. The emission points within synthetic ammonia plants include the natural gas desulfurization tank, the primary reformer, the carbon dioxide regenerator, and the condensate stripper. Materials emitted from synthetic ammonia plants include the criteria pollutants, reduced sulfur compounds, ammonia, monoethanolamine, and methanol.

Emission inventory data were supplied by plant personnel and by state EPA officials. There was no source testing performed to confirm the validity of the emissions inventory data. Table VII presents the emission factors for synthetic ammonia plants while Table VIII presents the estimated 1978 emissions inventory for synthetic ammonia production.

Ammonium Nitrate Manufacture

Ammonium nitrate is produced from ammonia and nitric acid. There are 64 plant sites with a total production capacity of 8.29×10^6 metric tons per year and they typically operate at 86% capacity. Ammonium nitrate is produced as a solution, as high density prills, and as low density prills. Emission points within ammonium nitrate production include the neutralizer, evaporator/concentrator, prill tower, cooler, predryer, dryer, cooler, and coating. Materials emitted include particulates (ammonium nitrate), ammonia, and nitric acid fume. Emissions of ammonia and nitric acid are determined by which material is present in excess in the neutralizer.

Emission inventory data were supplied by plant personnel. MRC did not perform source testing to confirm the data. Table IX presents the particulate emission factors for ammonium nitrate plants. The mass of particulate emissions from ammonium nitrate plants in 1978 is estimated to be 18,865 metric tons.

TABLE I. EMISSION FACTORS FOR ACRYLONITRILE MANUFACTURE BY EMISSION POINT (UNCONTROLLED EMISSIONS) (g/kg)

TABLE 1. EMISSION FACTORS FOR ACRYLONITRILE MANUFACTURE BY EMISSION POINT (UNCONTROLLED EMISSIONS)
(g/kg)

	Emission point					Storage tank emission point					
Material emitted	Absorber vent	Incinerator stack	Flare stack	Deep well pond	Fugitive emissions	Product transport loading facility	Two product acrylonitrile run-down tanks[b]	Three product acrylonitrile field storage tanks[b]	Off-specification acrylonitrile	Two crude acrylonitrile storage tanks[b]	Total
Pollutants											
Carbon monoxide	79.3 ± 6%	0.0040 ± 10%									79.3
Hydrocarbons (as CH_4)[a]	57.1 ± 7%	0.0203 ± 47%	0.268	13 ± 61%	0.00038 ± 20%	0.0055 ± 20%	0.039 ± 20%	0.17 ± 20%	0.025 ± 20%	0.024 ± 20%	71.06
Nitrogen oxides		0.542 ± 107% - 100%	0.01								0.552
Sulfur oxides		0.0176 ± 59%									0.0176
Particulates											
Chemical substances											
Methane	0.67 ± 6%	0.0023 ± 10%									0.6723
Ethane	1.93 ± 92%										1.93
Ethylene	2.57 ± 81%										2.57
Propane and Propylene	55.0 ± 60%		0.022		0.000006 ± 20%						55.0
Butene	0.400 ± 50%										0.400
Benzene	0.146 ± 50%										0.202
Toluene	0.065 ± 50%										0.074
Acrylonitrile	0.039 ± 41%	<0.0015	0.039		0.00042 ± 20%	0.0065 ± 20%	0.046 ± 20%	0.2 ± 20%	0.03 ± 20%		0.807
Acetonitrile	0.625 ± 49%	<0.0015			0.000024 ± 20%						0.687
Hydrogen cyanide	0.275 ± 22%	0.0341 + 428% - 100%	0.35							0.04 ± 20%	0.739
Fumaronitrile				0.036							0.018
Pyridine				5.2 ± 74%							2.58
Propionaldehyde	0.0061 ± 50%										0.0061
Furan	0.467 ± 50%										0.467
Ammonia					0.000006 ± 20%						0.000006
Allyl alcohol	0.024 ± 50%										0.024

[a] Emission factors for total hydrocarbons do not equal the sum of emission factors for all organic materials except methane. To determine the hydrocarbon emission, the methane equivalent emission factors (based on carbon) for each nonmethane organic material are calculated and then summed. (Statement applies to all emission points except deep well pond where 7.8 g/kg of material [two species] were unidentifiable).

[b] Values shown apply to each tank comprising the emission point.

Note: Blanks indicate no emissions present.

TABLE II. 1978 EMISSIONS INVENTORY FOR ACRYLONITRILE MANUFACTURE

Material emitted	1978 Emission rate, metric tons
Criteria pollutants:	
Carbon monoxide	26,900
Nonmethane hydrocarbons (as CH_4)	24,100
Nitrogen oxides (as NO_2)	187
Sulfur oxides (as SO_2)	6
Chemical substances:	
Methane	228
Ethane	655
Ethylene	872
Propane	1,700
Propylene	17,000
Butene	136
Benzene	69
Toluene	25
Acrylonitrile	274
Acetonitrile	233
Hydrogen cyanide	250
Fumaronitrile	6
Pyridine	875
Propionaldehyde	2
Furan	159
Allyl alcohol	8
Ammonia	<1

TABLE III. 1978 EMISSION FACTOR FOR PHTHALIC ANHYDRIDE PLANTS, g/kg

Material emitted	O-xylene process[a]		Naphthalene process[a]	
	Uncontrolled	Controlled	Uncontrolled	Controlled
Particulate				
Main process incinerator	-[b]	0.25 ± 50%	-[b]	0.25 ± 70%
Secondary incinerator	-[b]	0.125 ± 50%	-[b]	0.125 ± 70%
Flaker and bagger	0.10	0.001	0.10	0.001
Sulfur oxides				
Main process incinerator	5.0 ± 25%	5.0 ± 25%	-[h]	-[h]
Nitrogen oxides				
Main process incinerator	-[c]	1.25 ± 50%	-[c]	1.25 ± 70%
Secondary incinerator	-[c]	0.125 ± 25%	-[c]	0.125 ± 40%
Carbon monoxide				
Main process incinerator	125.0 ± 20%	0.125 ± 50%	50.5 ± 50%	0.05 ± 70%
Secondary incinerator	-[c]	1.25 ± 50%	-[c]	1.25 ± 70%
Maleic anhydride				
Main process incinerator	52.0 ± 20%	1.82 ± 25%	7.0 ± 200%	0.24 ± 200%
Secondary incinerator	3.75 ± 83%	0.038 ± 90%	4.9 ± 80%	0.05 ± 90%
Phthalic anhydride				
Main process incinerator	15.6 ± 20%	0.545 ± 25%	20.4 ± 40%	0.71 ± 50%
Secondary incinerator	10.6 ± 53%	0.106 ± 60%	9.8 ± 70%	0.10 ± 80%
Storage tanks	0.29 ± 10%	0.003 ± 20%	0.37 ± 10%	0.004 ± 20%
Flaker and bagger	0.10	0.001	0.10	0.001
Transport loading	0.45 ± 10%	0.005 ± 20%	0.45	0.005
Fugitive emissions	-[b]	-[d]	-[b]	-[d]
Benzoic acid				
Main process incinerator	3.12 ± 20%	0.109 ± 25%	1.56 ± 40%	0.05 ± 50%
Secondary incinerator	1.25 ± 50%	0.0125 ± 55%	-[b]	-[b]
Diphenyl oxide[e]				
Fugitive emissions	0.016	-[d]	0.016	-[d]
O-Xylene				
Storage tanks	0.20 ± 10%	0.002 ± 20%	-[h]	-[h]
Formaldehyde				
Main process incinerator	2.1[f]	0.074[f]	2.1[f]	0.074[f]
Secondary incinerator	-[b]		-[b]	-[b]
Total hydrocarbons[g]				
Main process incinerator	72.8 ± 30%	2.6 ± 30%	31.8 ± 79%	1.09 ± 85%
Secondary incinerator	18.8 ± 60%	0.16 ± 60%	26.5 ± 70%	0.27 ± 80%
Storage tanks	0.49 ± 10%	0.005 ± 20%	0.97 ± 10%	0.01 ± 20%
Flaker and bagger	0.1	0.001	0.1	0.001
Transport loading	0.45 ± 10%	0.005 ± 20%	0.45 ± 10%	0.005 ± 20%
Fugitive emissions	0.116	-[d]	0.116	-[d]
Naphthoquinone				
Main process incinerator	-[h]	-[h]	0.69 ± 40%	0.02 ± 50%
Secondary incinerator	-[h]	-[h]	6.6 ± 70%	0.07 ± 80%
Naphthalene				
Storage tanks	-[h]	-[h]	0.60 ± 10%	0.006 ± 20%
Vanadium oxide catalyst				
Catalyst storage	-[h]	-[h]	0.41	0.01
Fugitive emissions	-[h]	-[h]	-[b]	-[d]

[a] Emission factor is defined as weight of emission per unit weight of phthalic anhydride product.

[b] Emission data not available.

[c] No emissions generated in uncontrolled process.

[d] Fugitive emissions are not controlled.

[e] Heat-transfer fluid, assumed to be Dowtherm A.

[f] Total aldehydes reported as formaldehyde.

[g] Includes all nonmethane organic species.

[h] Not present in plant emissions.

TABLE IV. 1978 EMISSIONS INVENTORY FOR PHTHALIC ANHYDRIDE MANUFACTURE
metric tons/yr

Material emitted	*O*-Xylene process	Naphthalene process	Total
Criteria pollutants			
Particulate	130	63	193
Sulfur oxides (as SO_2)	1,700	-[a]	1,700
Nitrogen oxides (as NO_2)	460	230	690
Carbon monoxide	460	220	680
Nonmethane hydrocarbons (as CH_4)	940	18	958
Chemical Substances			
Maleic anhydride	630	48	678
Phthalic anhydride	220	140	360
Benzoic acid	40	8	48
Diphenyl oxide	5	-[a]	5
O-Xylene	1	3	4
Formaldehyde	25	12	37
Naphthoquinone	-[a]	15	15
Naphthalene	-[a]	1	1
Vanadium oxide catalyst	-	2	2

[a]Not present in plant emissions.

TABLE V. EMISSION FACTORS FOR A REPRESENTATIVE CARBON BLACK PLANT

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Material emitted	Emission factor,[a] g/kg: Main process vent		Dryer vent		Pneumatic system vent	Oil storage tanks	Vacuum cleanup system vent	Fugitive emissions
Criteria pollutants								
Particulate matter[b]	0.11	± 70%	0.12 ± 89%		0.3 ± 93%		0.03 ± 58%	0.1
Sulfur oxides	-[c]		0.23 ± 60%					
Nitrogen oxides	0.28	± 15%	0.60 + 200% - 100%					
Hydrocarbons[d]	50	± 48%				0.72 ± 10%		
Carbon monoxide	1,400	± 19%						
Hazardous materials								
Beryllium	2.2×10^{-6}	16%						
Mercury	1.5×10^{-4}	+ 386% - 100%						
Inert gases								
Nitrogen & argon	9,000	± 19%	2,200 ± 21%		N.A.[e]			
Oxygen	240	± 99%	400 ± 65%		N.A.			
Carbon dioxide	700	± 21%						
Chemical substances								
Hydrogen	120	± 39%						
Hydrogen sulfide	30	± 82						
Carbon disulfide	30	± 76						
Carbonyl sulfide	10	± 99%						
Carbon black	0.11	± 70%	0.12 ± 89%		0.3 ± 93%		0.03 ± 58%	0.1
Methane	25	± 47%						
Acetylene	45	± 48%						
Ethane	N.A.							
Ethylene	1.6	± 85%						
Propylene	-[c]							
Propane	0.23	+ 109% - 100%						
Isobutane	0.10	± 80%						
n-Butane	0.27	± 57%						
n-Pentane	N.A.							
POM (total)[f]	0.002	± 52%						
Trace elements (total)[g]	<0.25	± 43						

[a] Blanks indicate no emissions.

[b] The particulate matter is carbon black.

[c] Not detected at detection limit of 1 ppm.

[d] Total nonmethane hhdrocarbons. The individual hydrocarbon species are listed under chemical substances.

[e] Not available.

[f] Emission factors for individual POM species are given in Table 24, Section IV.B.

[g] Includes beryllium and mercury. Emission factors for individual trace elements are given in Table 25, Section IV.B.

TABLE VI. 1978 EMISSIONS INVENTORY FOR CARBON BLACK MANUFACTURE

Material emitted	1978 Emission rate, metric tons
Criteria pollutants	
Particulate	1,240
Sulfur oxides (as SO_2)	98,600
Nitrogen oxides (as NO_2)	1,280
Nonmethane hydrocarbons (as CH_4)	37,000
Carbon monoxide	1,040,000
Hazardous materials	
Beryllium	<0.01
Mercury	0.3
Chemical substances	
Hydrogen	2,260
Hydrogen sulfide	35,700
Carbon disulfide	35,700
Carbonyl sulfide	11,900
Carbon black	1,240
Methane	470
Acetylene	860
Ethane	150
Ethylene	22
Propane	21
Isobutane	9
N-butane	25
POM[a]	4
Trace metals	<470

[a] SO_2 is produced during the thermal oxidation of H_2S, COS and CS_2 in the control devices employed at carbon black plants.

[b] POM = polycyclic organic material.

TABLE VII. EMISSION FACTORS FOR SYNTHETIC AMMONIA PRODUCTION

Emission point	Emission species	Emission factor, g/kg
Desulfurization tank[a]	Total sulfur	0.0096[b,c]
	CO	6.9
	Hydrocarbons	3.6
Primary reformer		
Burning natural gas	NO_x	2.7 ± 23%
	SO_x	0.0024
	CO	0.068
	Particulates	0.072
	Hydrocarbons	0.012
Burning fuel oil	NO_x	2.7
	SO_x	1.3
	CO	0.12
	Particulates	0.45
	Hydrocarbons	0.15
Carbon dioxide regenerator	Ammonia	1.0
	CO	1.0
	Carbon dioxide	1,220
	Hydrocarbons	0.47
	Monoethanolamine	0.05
Condensate stripper	Ammonia	1.1 ± 4%
	Carbon dioxide	3.4 ± 60%
	Methanol	0.6 ± 2%

[a] Intermittent source of emissions; desulfurization tank is regenerated on the average once every 30 days for a 10-hr period.

[b] Worst case condition assuming all sulfur entering the tank is emitted during regeneration.

[c] Normalized to a 24-hr emission factor.

TABLE VIII. 1978 EMISSIONS INVENTORY FOR SYNTHETIC AMMONIA PRODUCTION

Material emitted	1978 Emission rate, metric tons
Criteria pollutants	
Carbon monoxide	121,000
Nonmethane hydrocarbons (as CH_4)	62,000
Nitrogen oxides (as NO_2)	41,000
Sulfur oxides (as SO_2)	20,000
Particulate	1,100
Chemical substances	
Reduced sulfur compounds	140
Ammonia	15,000
Monoethanolamine	760
Methanol	9,100

TABLE IX. PARTICULATE EMISSION FACTORS FOR AMMONIUM NITRATE PLANTS

Emission point	Emission factor,[a] g/kg
Solutions and high density prills	
Neutralizer[b]	1.64 ± 84%
Evaporator/concentrator[b]	0.47[c]
Prill tower[d]	1.37 ± 10%
Cooler[d]	0.05[c]
Low density prills[e]	
Neutralizer	0.045
Evaporator/concentrator	0.088
Prill tower	0.496
Predryer	0.015
Dryer	0.009
Cooler	0.016
Coating	3.0

[a] Emission factors are for uncontrolled operations except for predryer, dryer, and cooler.

[b] Parameters are based on an average neutralizer capacity of 131,500 metric tons/yr.

[c] Percent uncertainty not reported since value is determined by theoretical calculations.

[d] Parameters are based on average high density prilling capacity of 95,000 metric tons/yr.

[e] Parameters are based on average low density prilling capacity of 62,700 metric tons/yr.