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POLLUTANT REMOVAL HANDBOOK



POLLUTANT REMOVAL HANDBOOK

Marshall Sittig

NOYES DATA CORPORATION

Park Ridge, New Jersey

London, England

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FOREWORD

This Pollutant Removal Handbook attempts to clarify the ways and means open to the alert industrial processor who must keep his polluting wastes down to a minimum.

The book contains a total of 128 subject entries arranged in an alphabetical and encyclopedic fashion. Because of its encyclopedic arrangement, it can also serve as a textbook and professional aid to eager students in the fields of antipollution engineering and pollution abatement.

During the past few years, the words pollution, environment and ecology have come into frequent usage and the cleanliness of the world we live in has become the concern of all people. Pollution, for example, is no longer just a local problem involving litter in the streets or the condition of a nearby beach. Areas of the oceans, far-reaching rivers and the largest lakes are now classified as polluted or subject to polluting conditions. In addition, very surprisingly, lakes and streams remote from industry and population centers have been found to be contaminated.

For these reasons, this handbook gives pertinent and concise information on such widely divergent topics as the removal of oil slicks in oceans to the containment of odors and particulates from paper mills.

Aside from practical considerations such as indicating by its extensive bibliographical lists, further sources to consult for additional information, this book is also helpful in explaining the new lingo of pollution abatement. This field is developing new concepts and a new terminology all its own, for example, particulates, polyelectrolytes, flocculation, recycling, activated sludge, gas incineration, catalytic conversion, industrial ecology, etc.

Advanced composition and production methods developed by Noyes Data are employed to bring our new durably bound books to you in a minimum of time. Special techniques are used to close the gap between "manuscript" and "completed book." Industrial technology is progressing so rapidly that time-honored, conventional typesetting, binding and shipping methods are no longer suitable. We have bypassed the delays in the conventional book publishing cycle and provide the user with an effective and convenient means of reviewing up-to-date information in depth.

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INTRODUCTION

The purpose of this handbook is to provide a one-volume ready reference for the handling of pollutants, and particularly those pollutants emanating from industrial processes.

The major sources of the information contained herein are U.S. patents and U.S. Government reports, primarily from the Environmental Protection Agency. Through citations in these and other sources, however, hundreds of references to books and periodical literature are given here. Thus, this book provides a ready reference to the entire spectrum of published literature on pollutant removal. While all of this material is presumably available and in the public domain, in actual fact its location and abstracting may be a tedious, time-consuming and expensive process. Thus, this volume is specifically designed to save the concerned reader time and money in his or her search for pertinent information on the control of specific pollutants.

This book is addressed to the industrialist, to the local air pollution control officer, to legislators who are contemplating control measures, to the conservationist who is interested in exactly what can be done about the effluents of local factories, as well as to the student and concerned citizen.

As one specific set of references to complement this volume, the reader is referred to the series on pollution control, industry by industry, by H.R. Jones. The titles to date include:

Environmental Control in the Organic and Petrochemical Industries, 1971

Environmental Control in the Inorganic Chemical Industry, 1972

Pollution Control in the Nonferrous Metals Industry, 1972

Waste Disposal Control in the Fruit and Vegetable Industry, 1973

Pollution Control in the Textile Industry, 1973

Pollution Control and Chemical Recovery in the Pulp and Paper Industry, 1973.

All of these volumes have also been published by Noyes Data Corporation, Park Ridge, New Jersey.

ACIDS

Industrial wastes of many types, and from a variety of processes, exhibit extreme pH values which can greatly influence the quality and aquatic life of receiving waters. Table 1 lists some representative industries, and gives waste pH characteristics associated with each industry. Wastes may be released on a batch basis as acid processing vats are dumped, or released as a continuous waste stream resulting from a specific industrial process (e.g., rinsing). The volume and composition of a waste stream containing acidic compounds can be quite variable. Dickerson and Brooks (1) have described the waste stream from a cellulose production line of Hercules Powder Co. as varying in volume from 3,000 to 9,000 gpm with acidity, measured as free sulfuric acid, ranging from 30 to 1,100 mg./l.

The problem of acid waste disposal has also been addressed by Cooper (2).

The reader of this handbook is referred to specific sections which follow on Hydrogen Chloride, Phosphoric Acid and Sulfuric Acid.

TABLE 1: pH CHARACTERISTICS OF INDUSTRIAL WASTES (3)

Industrial Process	Waste pH Characteristics
Food and Drugs:	
Pickling	Acidic or alkaline
Soft Drinks	High pH
Apparel:	
Textile	Highly alkaline
Leather Processing	Variable
Laundry	Alkaline
Chemicals:	
Acids	Low pH
Phosphate and Phosphorus	Low pH
Materials:	
Pulp and Paper	High or low pH
Photographic Products	Alkaline
Steel	Mainly acid, some alkaline
Metal Plating	Acids
Oil	Acids
Rubber Stores	Variable pH
Naval Stores	Acid
Energy:	
Coal Processing	Low pH

Source: Report PB 204,521

Removal of Acids from Air

See under removal of specific acids from air, for example: Aromatic Acids and Anhydrides, Hydrogen Chloride, Hydrogen Fluoride, Phosphoric Acid, Sulfuric Acid.

Removal of Acids from Water

Methods include: [1] mixing acid and alkaline wastes so that the net effect is a near-neutral pH; [2] passing acid wastewaters through beds of limestone; [3] mixing acid wastes with lime slurries or dolomite lime slurries; [4] adding the proper amounts of concentrated caustic soda (NaOH) or soda ash (Na_2CO_3) to acid wastewaters; [6] bubbling waste boiler-flue gas through alkaline wastes; [7] adding strong acid to alkaline wastes, according to Patterson et al (4).

The selection of a caustic agent to neutralize an acid waste is usually between sodium

hydroxide (caustic soda, NaOH), sodium carbonate (soda ash, Na_2CO_3) and various limes (calcium oxide compounds). The important factors in selection of a caustic reagent include purchase price, neutralization capacity, storage and equipment costs, and neutralization end products. The costs of the various caustic reagents have been summarized by Ross (5). Although sodium hydroxide is far more expensive than the other materials, it is frequently selected due to composition uniformity, ease of storage and feedings, rapid reaction rate, and solubility of end products. Sodium carbonate is not as reactive as sodium hydroxide and can produce foaming problems due to release of carbon dioxide.

Hansen (6) has reported the use of both sulfuric acid and hydrated lime, $\text{Ca}(\text{OH})_2$, in treating a metal finishing waste. Both acid and alkaline wastes were produced in the industrial process, and an effluent pH of approximately 9.0 was routinely achieved. It has been pointed out that acid wastes which contain iron salts, as most metal plating and ferrous industry wastes do, may require 3 to 10 times the amount of neutralizing caustic agent required by acidic solutions of equivalent pH which do not contain the iron salts as discussed by Ormya (7). MacDougall (8) has also discussed the problem associated with the presence of acidic iron salts in acid wastes. He reports that waste sulfuric acid, used in cleaning rust from steel products, typically contains 2 to 7% (or 2,000 to 7,000 mg./l.) free acid, and 15 to 22% ferrous sulfate (an acid salt).

As discussed above, salts of weak acids or bases influence the pH of effluents and receiving waters, and exert a chemical demand for additional neutralizing agent.

K.S. Watson (9) has summarized the treatment efficiency and neutralizing agent demand for an acid waste originating from cleaning, plating and other metal-finishing operations of a General Electric Company plant. The acid waste was over-neutralized to an alkaline pH, in order to allow later precipitation of waste heavy metals. Thus the large quantities of lime used resulted from four requirements: [1] neutralization of the free acids; [2] neutralization of the combined acids (i.e., acid salts); [3] over-neutralization to an alkaline pH, in order to achieve conditions suitable for heavy metal-hydroxide precipitation; and [4] the lime required to react with the heavy metals, forming insoluble hydroxides.

Because of the high lime demand, operating costs of this acid waste treatment process were extremely high at \$26.20 per 1,000 gallons, in contrast to the usual 10 to 20¢ per 1,000 gallons required for simple acid/alkaline neutralization, described by Zievers et al (10). Total treatment costs, including equipment depreciation, were \$65.50 per thousand gallons. The author points out that acid treatment costs are high because the acid waste is comparatively concentrated, and considerable lime is required for the neutralization. Capital cost of the acid waste treatment facility was \$106,387, exclusive of the waste collection system, according to Watson (9).

References

- (1) Dickerson, B.W. and Brooks, R.M., "Neutralization of Acid Wastes," *Ind. Eng. Chem.* 42, 599-605 (1950).
- (2) Cooper, J.E., "How to Dispose of Acid Wastes," *Chemistry and Industry* 1950, 684-685.
- (3) Nemerow, N.L., *Theories and Practices of Industrial Waste Treatment*, Reading, Mass., Addison-Wesley Publishing Co. (1963).
- (4) Patterson, J.W. and Minear, R.A., "Wastewater Treatment Technology," *Report PB 204,521*, Springfield, Va., National Technical Information Service (Aug. 1971).
- (5) Ross, R.D., *Industrial Waste Disposal*, New York, Reinhold Book Corp. (1968).
- (6) Hanson, N.H., "Design and Operation Problems of a Continuous Automatic Plating Waste Treatment Plant at the Data Processing Division, IBM, Rochester, Minn.," *Proc. 14th Purdue Industrial Waste Conf.*, pp. 227-249, 1959.
- (7) Ormya, S.A., "Treatment of Residual Acid Effluent," *Wat. Waste Treatment* 12, 27-28, 1968.
- (8) MacDougall, H., "Waste Disposal at a Steel Plant: Treatment of Sheet and Tin Metal Wastes," *ASCE Separate No. 493*, September, 1954.
- (9) Watson, K.S., "Treatment of Complex Metal-Finishing Wastes," *Sew. Industr. Wastes* 26, 182-194, 1954.
- (10) Zievers, J.F., Crain, R.W. and Barclay, F.G., "Waste Treatment in Metal Finishing: U.S. and European Practices," *Plating* 55, 1171-1179 (1968).

ADIPIC ACID

Adipic Acid Removal from Wastewater

A process developed by C.R. Campbell, D.E. Danly and M.J. Mathews III (1) is a process for the removal of monobasic and dibasic acids, mineral acids, and other organic and inorganic material from aqueous mixtures prior to the discharge thereof to waste.

An example of a commercially important chemical process which gives rise to a waste disposal problem is the production of pure dibasic acids by the oxidation of cycloparaffins. This process is of considerable commercial importance because of the extensive and expanding use of such acids in the preparation of polyamide resins and because of the ready availability of cyclic hydrocarbons as starting materials from which the acids may be made. Much art is known and available which describes processes for the direct oxidation of cycloparaffins to a variety of products including a mixture of monobasic and dibasic acids. Improvements in the processes known in the art have shown that yields of individual dibasic acids can be increased markedly when the oxidation is carried out in stages in which the cycloparaffins are air oxidized first to corresponding cyclic alcohols and ketones, and then the mixture of alcohols and ketones is nitric acid oxidized to a mixture of corresponding dibasic acids.

In the more sophisticated oxidation processes only selective portions of the air oxidation product are subjected to nitric acid oxidation, and mixtures of monobasic and dibasic acids are obtained which contain predominate amounts of a single dibasic acid and only minor amounts of other monobasic and dibasic acids. In accordance with this two-step oxidation process, cycloparaffins are first air oxidized and a selective part of the air oxidation product is nitric acid oxidized to give mixture of monobasic and dibasic acids predominant in one dibasic acid in an aqueous nitric acid solution. Either this aqueous mixture or the mother liquor remaining after crystallization of a portion of the predominant dibasic acid therefrom is subjected to evaporating conditions to reduce the nitric acid concentration of the liquor, and further crystallization of the predominant dibasic acid is effected.

The mother liquor from this second crystallization contains additional dibasic acids which cannot be crystallized successfully, and therefore, the mixture of dibasic acids contained in this second mother liquor or the mixture remaining after a second evaporation to reduce the nitric acid concentration may be separated, if desired, from each other in excellent yields by treatment with a suitable immiscible solvent or other means to permit recovery of substantially all the dibasic acids contained therein.

An example of such a process is the manufacture of adipic acid by the air oxidation of cyclohexane followed by the nitric acid oxidation of a selective portion of the air oxidation product. In this process the aqueous nitric acid mixture resulting from nitric acid oxidation is predominantly adipic acid and contains other dibasic acids such as glutaric and succinic as well as monobasic acids.

An example of a waste aqueous stream which is high in chemical oxygen demand and which cannot be discharged safely without treatment is the aqueous mixture which results from the overhead or make stream from the evaporation, either before or after crystallization of adipic acid, of the aqueous product of the nitric acid oxidation described above.

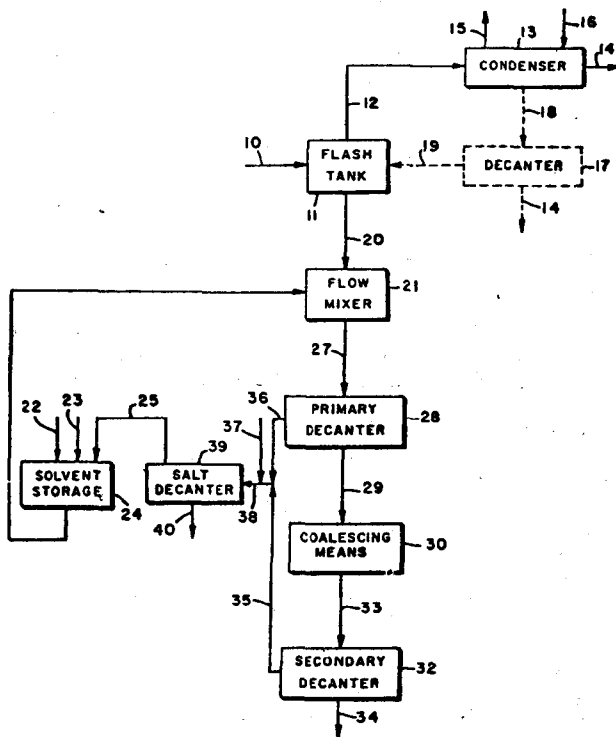
In this process, the aqueous mixture described above, or any similar aqueous mixture, is contacted either in single or multiple stages with a liquid ion exchange material dissolved in a suitable solvent to remove the chemical oxygen demand causing components in the solvent phase, thereby leaving purified water suitable for safe, nonchemical polluting waste discharge to rivers or other natural waste areas. The resulting solvent phase may be contacted with an inorganic base, anhydrous ammonia, an aqueous solution of an inorganic base or ammonia, or mixtures thereof to regenerate the solvent solution of ion exchange material for recycle or other use, and the remaining concentrated aqueous solution of salts of the organic acids and other chemical oxygen demand causing components which remain

in much reduced volume may be disposed of by incineration or other suitable nonpolluting means or recovered for profitable use. Figure 1 is a block flow diagram showing the essentials of this process.

The aqueous solution from which the high chemical oxygen demand material must be removed prior to the discharge of the water to waste enters the process at 10. In the example of the aqueous mixture for which the process will be described, the nitric acid concentration of this aqueous mixture may be from 0 to 1% by weight of the water therein; however, generally the nitric acid concentration may be between 0.05 and 0.5% by weight. The water-soluble organic acid concentration of this aqueous mixture may be from 0 to 5.0% by weight of the water therein, however, generally may be between 0.1 and 3.0%.

Nonacidic organic liquids which may be entrained in the aqueous mixture to be purified and which may operate as a solvent or ion exchange resin contaminant, both of which will be described later, may be flashed overhead in flash tank 11, with heat supplied by a source, not shown, or these organic liquids may be removed by any other means such as decanting or other. The overhead stream, as indicated at 12, may be condensed in condenser 13 and discharged to a sump or other as indicated by line 14. Cooling water for condenser 13 enters at 16 and exits at 15.

FIGURE 1: BLOCK FLOW DIAGRAM FOR PURIFICATION OF WASTEWATERS CONTAINING ADIPIC ACID



Source: C.R. Campbell, D.E. Danly and M.J. Mathews III, U.S. Patent 3,267,029; August 16, 1966

As an example, cyclohexyl nitrate may be present in the described aqueous mixture to be purified in a concentration up to 4,000 parts per million, and since this material will concentrate in the immiscible solvent, causing continuing dilution of the ion exchange resin, the cyclohexyl nitrate may be flashed overhead with a portion of the water by introducing waste process steam into feed line 10 or into flash tank 11.

If it is desired to reduce the volume of liquid flowing in line 14, decanter 17 may be provided. If the process is operated in this manner all or a part of the liquid condensed in condenser 13 may proceed, as indicated by line 18 to decanter 17 where the liquid is permitted to separate into an aqueous layer and a water-immiscible layer with the aqueous layer being returned to the process, as indicated by line 19, and the water-immiscible layer being discharged to a sump or other suitable waste disposal means, as indicated by 14.

Ion exchange resin and solvent are introduced to the process, as indicated by lines 22 and 23 respectively, and a solvent solution of the ion exchange resin may be prepared by mixing or other means and maintained for use in the process in solvent storage 24. In operation or after a sufficient quantity of solvent solution of ion exchange resin has been prepared, only minor quantities of solvent and ion exchange resin may be added to the process by their respective lines to provide makeup with the major quantity of solvent for the process being provided by recycled regenerated solvent solution of ion exchange resin as indicated by line 25.

The ion exchange resin may be liquid or a solid capable of forming a solution, and may be any one of a mixture of more than one of any of a number of commercially available mixtures of high molecular weight primary, secondary or tertiary amines. Several of such ion exchange resins are marketed under the trademark Amberlite by Rohm and Haas Company with the designation LA-1 and LA-2.

The solvent used as carrier for the ion exchange resin may be any organic liquid material or mixture of organic liquid materials miscible with the ion exchange resin but substantially immiscible with water, such as xylene, benzene, mixed aromatic organic liquids having more than 9 carbon atoms, and kerosene.

The ion exchange resin and the solvent may be mixed in any manner such as mechanical stirring or flow mixing, and the concentration by weight of the ion exchange resin in the solvent may be between 1 and 100% with the preferred concentration range being between 10 and 30% by weight.

In the example of the process being described, the solvent may be either kerosene or xylene with kerosene being preferred, and the concentration of the Amberlite LA-2 in the kerosene or xylene may be 25% by weight. The solvent solution of ion exchange resin proceeds to flow mixer 21, as indicated by line 26, where it is mixed with the aqueous mixture, indicated entering flow mixer 21, by line 20.

The flow mixing of the solvent solution and the aqueous mixture may be accomplished by any suitable means which will provide good contacting of the solvent solution of ion exchange resin and the aqueous mixture for good extraction efficiency, but will not cause a dispersion of solvent solution in the aqueous mixture that is extremely slow in separating in subsequent steps of the process. As an example, in the embodiment being described, pumping of the solvent solution and the aqueous mixture may introduce sufficient energy to form a tight emulsion which is extremely difficult to separate and may require excessive holdup periods to separate into two phases. Proper mixing may be obtained by using a ball-type mixing valve and controlling the pressure drop across the valve. The amount of the pressure drop which is necessary and suitable is dependent upon the solvent used and the aqueous mixture to be purified, as well as other factors; and in the embodiment of the process being described, the pressure drop may be controlled at 1 lb./in².

The solvent solution to aqueous mixture ratio which is necessary is dependent upon many factors such as the chemical oxygen demand of the aqueous mixture or its acidity, the

concentration of the ion exchange resin in the solvent, and others. It has been found in the embodiment being described that when the acidity of the aqueous mixture is not in excess of 1.0 normal, the ratio of equivalents of ion exchange resin in the solvent to equivalents of acidity in aqueous mixture may be as low as 0.75 with good purification results being obtained. As is clear to those skilled in the art, the ratio of solvent solution of ion exchange resin to the aqueous mixture may be adjusted accordingly depending upon the ion exchange resin concentration in the solvent and the acidity of the aqueous mixture.

After mixing, the combined mixture of ion exchange resin solution and aqueous mixture proceeds, as indicated by line 27, to primary decanter 28 where the combined mixture is permitted to separate into an immiscible solvent phase and an aqueous phase. Primary decanter 28 may be of any design well known and suitable for the separation of two-phase systems and should be of sufficient size to provide adequate holdup time in the process to permit good separation of the immiscible solvent phase and the aqueous phase. In the described example, it has been found that the holdup time for good separation of the kerosene or xylene phase from the aqueous phase should be no less than five minutes to prevent entrainment of the aqueous phase in the solvent phase or excessive carryover of the solvent phase in the aqueous phase.

The aqueous phase containing a small amount of nonseparated solvent proceeds, as indicated by line 29, to coalescing means 30 where the solvent phase which did not separate in primary decanter is coalesced to assist in its separation in secondary decanter 32. Any suitable coalescing media such as sand or other may be used in coalescing means 30, and in the process of the example, 10 to 20 mesh sand in a bed 6 ft. high may be used successfully as the coalescing media at mass flow rates at least as high as 4,500 lbs./hr./sq. ft.

After passing through coalescing means 30, the aqueous phase proceeds, as indicated by line 33, to secondary decanter 32 where the final separation of the aqueous and immiscible solvent phases is permitted to take place. The secondary decanter should be sufficiently large to provide adequate holdup time for good separation or the inlet to the vessel may be sufficiently large to provide sufficient deceleration of the velocity of the material prior to its entry into the main body of the decanter to provide good separation in a smaller vessel. In the process of the example, it has been found that a vessel sufficiently large to provide a separating holdup time of 2 to 4 minutes for the liquid is adequate provided the inlet to the vessel is such that fluid velocities are about 0.3 to 2.5 ft./sec.

After separation of the phases in secondary decanter 32, the resulting aqueous phase which is now substantially free of chemical oxygen demand material may be discharged safely to any river, pond or other without danger of pollution, as indicated by line 34. The resulting immiscible solvent phase may be joined, as indicated by line 35, with the immiscible solvent phase leaving primary decanter 28, as indicated by line 36, for recovery and regeneration of the solvent solution of ion exchange resin.

Regenerating material is added to the immiscible solvent phase, as indicated by line 37, and this mixture proceeds, as shown by line 38, to decanter 39 where the regenerated solvent solution of ion exchange resin is separated either from an aqueous phase or a precipitate and returned to solvent storage 24, as indicated by line 25. The aqueous phase or the precipitate formed in the regeneration is removed from the process as indicated by line 40.

The regenerating material added as indicated at 37 may be an inorganic base, anhydrous ammonia, an aqueous solution of an inorganic base or ammonia, or mixtures thereof. If an aqueous solution of an inorganic base or ammonia is used, an aqueous phase is separated from the solvent solution of the ion exchange resin in decanter 39 and removed at 40; and if anhydrous ammonia or an inorganic base is used, a precipitate is separated and removed.

Contacting of the spent immiscible solvent phase of lines 35 and 36 with the regenerating material of line 37 may be accomplished by any suitable means that is convenient and efficient, and in the example of the process being described, contacting of the aqueous

ammonia, which may be the regenerating material, and the spent immiscible solvent solution may be effected in a recirculating centrifugal pump.

As is clear to those skilled in the art, care must be taken in controlling the amount of regenerating material added to the process. If insufficient regenerating material is added, the ion exchange resin solution will not be regenerated completely and the efficiency of the process will be reduced; and if an excessive amount of regenerating material is added, it will be returned to the process along with the solvent solution where it will prevent preferentially the ion exchange material from effecting efficient removal of the chemical oxygen demand material from the aqueous stream to be treated. In the example being described, a slight excess of the stoichiometric amount of ammonia needed to neutralize the chemical oxygen demand material in the solvent solution may be used.

The results of a typical operation of a single-stage process on a continuous basis according to the preferred embodiment are summarized below; all numbers are in pounds per hour unless otherwise specified. The column identified as "Feed" is line 10 in Figure 1, and the column identified as "Product" is line 34.

	Feed	Product
Water	100,000	97,137
Nitric Acid	287	0
Organic Acids	729	176
Ammonium Salts	0	22
Solvent	0	9
Cyclohexyl nitrate	49	5

As can be seen clearly from the above results, all of the inorganic acid and approximately 76% of the organic acids can be removed simply by the single-stage process. It is clear, also, that multistage purification by the use of this process can be accomplished easily if it is desired to reduce the chemical oxygen demand of the product below that which is possible with the use of a single stage.

References

- (1) Campbell, C.R., Danly, D.E. and Mathews, M.J. III, U.S. Patent 3,267,029; August 16, 1966; assigned to Monsanto Company.

ALDEHYDES

The most characteristic and important effect of aldehydes, particularly of low molecular weight aldehydes, for both humans and animals is primary irritation of the eyes, upper respiratory tract, and skin. The observed symptoms in humans from inhalation of low concentrations of aldehydes include lacrimation, coughing, sneezing, headache, weakness, dyspnea, laryngitis, pharyngitis, bronchitis, and dermatitis. In most cases, the general and parenteral toxicities of these aldehydes appear to be related mainly to these irritant effects. The unsaturated aldehydes are several times more toxic than the corresponding aliphatic aldehydes. Also, the toxicity generally decreases with increasing molecular weight within the unsaturated and aliphatic aldehyde series. Sensitization has occurred from contact with formaldehyde solutions and other aldehydes, but sensitization of the pulmonary tract rarely is produced by inhalation of aldehydes. The anesthetic properties of aldehydes are generally overshadowed by the stronger irritant effects. Furthermore, concentrations that can be tolerated via inhalation can usually be metabolized so rapidly that systemic symptoms do not occur.

Formaldehyde concentrations as low as 600 $\mu\text{g}/\text{m}^3$ have been shown to cause cessation of the ciliary beat in rats. Animal experiments have shown that aldehydes can affect the responses of the respiratory system, causing such effects as an increase in flow resistance

and in tidal volume and a decrease in the respiratory rate. Exposure of rats to 150 μg . per m^3 of acrolein for two months caused a rise in the number of luminescent leukocytes in the blood. Exposure of animals to high concentrations of aldehydes has been shown by several investigators to produce edema and hemorrhages of the lungs and fluid in the pleural and peritoneal cavities. In a Russian study, formaldehyde was found to prolong the mean duration of pregnancy in rats and decrease the number of offspring. In addition, the weight of the lungs and liver of the offspring was less than that of the controls' offspring, but other organs exhibited an increase in weight.

Animal experiments also indicate possible synergistic effects between aldehydes and aerosols. Thus, acrolein and formaldehyde in the presence of certain inert aerosols appeared to be more toxic to mice than the pure compounds. Experiments with guinea pigs showed that formaldehyde with sodium chloride aerosols produced significant increases in the "respiratory work" compared with the effect of the pure vapor.

In addition, to the toxic effects, aldehydes may contribute to the annoyances of odor and eye irritation caused by polluted air. Aldehyde concentrations have been shown to correlate with the intensity of odor of diesel exhaust and the intensity of eye irritation during natural and chemically produced smog. Data indicate that as little as 12 $\mu\text{g}/\text{m}^3$ of formaldehyde can cause human eye response.

Aldehyde air pollution may result in oxidant-type damage to plants, although atmospheric photochemically produced products from the aldehydes may actually cause the damage rather than direct attack by aldehydes. There are no data available to indicate the effect of aldehyde air pollution on materials.

Vehicle exhaust, particularly from automobiles, appears to be the major emission source of aldehydes. However, significant amounts may also be produced from other combustion sources such as open burning and incineration of solid waste materials, and the burning of fuels (gas, fuel oil, coal). Another source of aldehyde emission is the thermal decomposition of hydrocarbons by pyrolysis in the presence of air or oxygen. Sources of these emissions include chemical manufacturing plants and industries that use drying or baking ovens to remove organic solvents in such processes as automobile painting and the manufacture of coated paper and metals.

Air sampling data indicate that plants manufacturing formaldehyde may be local sources of aldehyde pollution; over 4 billion pounds of formaldehyde were manufactured in the United States in 1968. However, the major amount of aldehyde pollution in some areas of the United States is from the photochemical reaction between nitrogen oxides and hydrocarbons. Hydrocarbons that yield formaldehyde are olefins, and to a lesser degree, other aldehydes and aromatic hydrocarbons. Diolefins produce most of the atmospheric acrolein. Some data indicate that in certain areas over two-thirds of the atmospheric aldehydes may have resulted from photochemical reactions. Of course, the sources that emit aldehyde pollutants are generally the same as those emitting hydrocarbons and nitrogen oxides.

In addition, aldehydes themselves may undergo photochemical reactions. They may produce, at low partial pressure in the presence of nitrogen oxides, other products such as carbon monoxide, lower aldehydes, nitrates, and oxidants. The oxidants produced include ozone, peroxyacyl nitrates, and alkyl hydroperoxides (hydrogen peroxide in the case of formaldehyde). No peroxyacids or diacetyl peroxides are found at low partial pressure of aldehydes.

In 1967 the National Air Sampling Network began to report data for aliphatic aldehydes. The data for 1967 for several cities show that the average concentrations of aldehydes ranged from 3 to 79 $\mu\text{g}/\text{m}^3$ and that the maximum values ranged from 5 to 161 $\mu\text{g}/\text{m}^3$. A Los Angeles area report indicates that the maximum values for two "smog" days in 1968 were 208 $\mu\text{g}/\text{m}^3$ for aliphatic aldehydes, 163 $\mu\text{g}/\text{m}^3$ for formaldehyde, and 27 $\mu\text{g}/\text{m}^3$ for acrolein. Generally, formaldehyde accounts for 50% or more of the total aldehydes, while

acrolein accounts for about 5%, according to Q.R. Stahl (1).

Removal of Aldehydes from Air

Control methods for the removal of aldehydes from air streams, as reported by Stahl (1) include more effective combustion methods and the use of direct-flame and catalytic afterburners. Paradoxically, although these methods generally decrease the amount of emissions, they may actually produce greater amounts of aldehydes and other oxygenated hydrocarbons from the burning of streams containing a variety of organic compounds.

Table 2 shows reported aldehyde emissions from various sources. As noted there, the amount of aldehydes increases tenfold by the use of afterburners in some drying oven processes.

TABLE 2: REPORTED ALDEHYDE EMISSIONS FROM VARIOUS SOURCES

Source	Aldehyde Emissions (as formaldehyde)	Reference
Amberglass Manufacture		
Regenerative furnace, gas fired	8,400 $\mu\text{g./m.}^3$	2
Brakeshoe Debonding (single-chamber oven)	0.10 lb./hr.	2
Core Ovens		
Direct gas fired (phenolic resin core binder from oven)	62,400 $\mu\text{g./m.}^3$	2
Direct gas fired (linseed oil core binder from afterburner)	<12,000 $\mu\text{g./m.}^3$	2
Indirect electric (linseed oil core binder from oven) (from afterburner)	189,600 $\mu\text{g./m.}^3$ <22,800 $\mu\text{g./m.}^3$	2
Insulated Wire Reclaiming, covering		
Rubber $5/8"$ o.d.	126,000 $\mu\text{g./m.}^3$	2
Secondary burner off	6,000 $\mu\text{g./m.}^3$	2
Cotton-Rubber-Plastic $3/8$ - $5/8"$ o.d.		
Secondary burner off	10,800 to 43,200 $\mu\text{g./m.}^3$	2
Secondary burner on	4,800 $\mu\text{g./m.}^3$	2
Meat Smokehouses		
Pressure mixing burner		
Afterburner inlet	0.04 lb./hr.	2
Afterburner outlet	0.22 lb./hr.	2
Multijet burner		
Afterburner inlet	0.49 lb./hr.	2
Afterburner outlet	0.22 lb./hr.	2
Meat Smokehouse Effluent, gas fired boiler-firebox as "afterburner"		
Water-tube, 426 hp.		
Afterburner inlet	0.22 lb./hr.	2
Afterburner outlet	0.09 lb./hr.	2
Water-tube, 268 hp.		
Afterburner inlet	0.39 lb./hr.	2
Afterburner outlet	0.40 lb./hr.	2
Water-tube, 200 hp.		
Afterburner inlet	0.39 lb./hr.	2
Afterburner outlet	0.30 lb./hr.	2
Locomotive, 113 hp.		
Afterburner inlet	0.03 lb./hr.	2
Afterburner outlet	0.0 lb./hr.	2
HRT, 150 hp.		
Afterburner inlet	0.03 lb./hr.	2
Afterburner outlet	0.18 lb./hr.	2

(continued)