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ATMOSPHERIC EMISSIONS from PAINT and VARNISH OPERATIONS

Part I

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PRESENT day protective coatings are the products of precisely controlled chemical reactions and accurately proportioned formulations which may include natural or synthetic drying oils, resins, pigments, volatile solvents, liquid driers, plasticizers, metallic soaps or anti-oxidants. A major component of most coatings is the synthetic resin vehicle, the manufacture of which may involve subjecting one or more complex organic materials to chemical reaction at elevated temperatures in order to attain the properties desired for a particular application. During these reactions, or cooking operations, there is some decomposition of the basic constituents with the result that a portion of the kettle ingredients is vaporized or otherwise lost to the surrounding atmosphere to be carried off in the form of gases, liquids and solids. Other atmospheric losses in this industry result from (1) the hot or cold thinning of lacquers, varnishes, resins and oils with volatile solvents and thinners to provide a proper consistency to the intermediate or end product, and (2) the storage or handling of both raw materials and intermediate products.

Because of the large volume and wide variety of oils and resins produced, and because of the type and amount of materials lost to the atmosphere during the high temperature cooking processes, the production of paint and varnish vehicles establishes itself as the principal source of atmospheric pollution in this industry. The term "fumes" is commonly applied to these cooking losses. Since recovery of these fumes has so far proven uneconomical, they are usually collected by hoods, enclosures and duct systems and are discharged to the outside air either directly or after some degree of treatment. Many of the chemicals discharged are undesirable as atmospheric constituents, and fall into the category of air pollutants. Under certain atmospheric conditions the undesirable quality of some pollutants in the air is compounded by chemical interaction and is intensified by sunshine. Increasing concern of health officials regarding air pollution and the growing demands by the general public for increased air pollution controls make it desirable to review some of the problems and considerations involved in determining the type and degree of air pollution controls which are or may be required in this industry.

This series is based on a review prepared at the request of the National Paint, Varnish & Lacquer Association by the U. S. Department of Health, Education, and Welfare, Public Health Service, Bureau of State Services, Division of Sanitary Engineering Services, at the Robert A. Taft Sanitary Engineering Center in Cincinnati, Ohio.

Part I is concerned with the sources of atmospheric pollution covering the cooking processes, mixing and thinning processes, and other miscellaneous sources. Part II, scheduled for our October issue, will discuss methods of controlling atmospheric emissions.

Reasons for Control

Although the immediate health effects of air pollutants are of prime importance in establishing the need for air pollution control, other factors include aesthetic considerations of man's environment and damage to vegetation and property. The situation requiring control of undesirable atmospheric emissions may vary from plant to plant and from locality to locality. Control may be voluntary or it may by enforced as a result of a legalized air pollution control agency, public pressure, or court order. Following are the specific conditions which may require air pollution control at a given plant:

Toxic Materials

The discharge of gases, vapors, or particulates into the atmosphere which are toxic or otherwise injurious to humans, animals or vegetation will obviously require immediate control.

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Smoke and Dust

Smoke and fly ash from combustion processes have long been recognized as undesirable atmospheric components. Most air pollution control ordinances specifically limit the discharge of these materials into the atmosphere.

Objectionable Odors

Whenever materials having objectionable odors are discharged to the atmosphere, they create an undesirable environment. A malodorous material need not be injurious to health to be considered undesirable. For legal purposes, odors are generally classified as nuisances, and ordinances prohibiting nuisances exist at almost every level of government. Ample evidence exists to indicate the attitude of courts in holding creators of odor nuisances responsible for the control of such odors. A number of the organic raw materials used in the protective coatings industry, and many of the decomposition and distillation by-products from such processes as heat polymerization and esterification of oils and resins, have highly disagreeable odors. The reduction or elimination of these odors is the principal reason that control of atmospheric emissions is required of this industry.

Property Damage

Materials discharged to the atmosphere may be chemically active liquids, solids or gases capable of reacting with such construction materials as stone, brick, cement, metals and surface coatings. Their effects will often be most noticeable on structures and automobiles immediately adjacent to the plant where they are discharged. One example of property damage resulting from vehicle production is the cooking of drying oils with phthalic anhydride. Water scrubbed fumes from the varnish kettles have been known to condense and freeze on the inside of exhaust ducts. With warming of the metal ducts, the ice breaks loose and becomes finely pulverized on passing through the exhaust fans. As a result, a fine aerosol of ice particles containing phthalic anhydride is discharged to the atmosphere and cars parked in the vicinity of the plant may suffer extensive pitting of the exterior paint as these particles settle.

Smog Formation

The atmospheric phenomenon commonly known as "smog" results from a combination of factors including the irradiation of atmospheric pollutants under proper meteorological conditions. While this process is not yet entirely understood, the materials presently thought to be of greatest importance in producing "smog" include oxides of nitrogen, unsaturated hydrocarbons (particularly olefinic) and ozone. Smog is most likely to occur in areas where a variety of chemical industries discharge large quantities of hydrocarbons to the atmosphere. Stagnant meteorological conditions which permit the concentration of pollutants to build up in the atmosphere and simultaneously provide a lengthened atmospheric reaction time appear to be additional factors conducive to smog formation.

Degree of Control Required

When odor problems are involved, the degree of control required may depend much on plant location. For example, objectionable odors emanating from a plant in or near a residential area will eventually become the object of complaints which sooner or later force the plant to effect sufficient controls to stop the complaints. Another plant using the same raw materials and manufacturing processes but in a less populated or strictly industrial location may get by without the need for controlling their emissions simply because the discharged material undergoes sufficient dilution to render the odors much less noticeable by the time they reach populated areas.

Sources of Atmospheric Pollution

Except for pigments, the majority of materials used in the manufacture of protective coatings are of organic composition with varying degrees of volatility; therefore, their storage, handling, mixing, and processing will produce different amounts of atmospheric pollution depending on the particular raw materials used, the combinations in which they are mixed, and the conditions to which they are subjected. Coatings are individually developed to satisfy an unusually wide variety of applications, and the basic vehicle is compounded to acquire special properties by adjusting both its chemical composition and the cooking procedure required for its production. As a result there are innumerable combinations of organic mixtures and time-temperature cooking procedures being used in the industry.

Cooking Processes

In the manufacture of paint and varnish vehicles, cooking is employed for bodying natural and synthetic oils: for the preparation of straight and oil-modified alkyds for processing short, medium and long oil varnishes: for polymerizing acrylic monomers: and for the conditioning of many other products. Through such reactions as oxidation, polymerization and esterification, the raw materials are transformed, by the application of heat, from their previous states to varying consistencies and compositions. Commonly used natural oils include linseed, soybean, perilla, tall, castor, oiticica, fish, and tung, while chemicals may include glycerine, phthalic anhydride, litharge, fumaric acid, pentaerythritol, various resins including rosin and many other substances depending on the process involved and the properties required of the final product. Cooking temperatures range from 200°F. up to 600°F. and are ordinarily maintained for several hours. Eight to twelve hours is an average length of cook, although some processes require heating for as long as 24 hours.

Decomposition of the kettle ingredients by vaporization, cracking, destructive distillation and chemical reaction produces fuming. This starts at around 350°F. in the average oil or varnish kettle. The rate of fuming rises with temperature increase and reaches its maximum when or shortly after the highest processing temperature is reached. Fuming continues so long as heating is continued. Gases so released may combine with solid or liquid particles by absorption or adsorption. Liquid droplets may become entrained in bubbles leaving the reactant to be picked up by the gas or air stream passing over the kettle. Solid particles may escape in the form of dust, as wetted particles in liquid droplets, or, if soluble, as droplets of solution.

Process and temperature	Kettle ingredients	Compounds identified	Odor
Heat polymerization of Linseed oil 575°F.	Linseed oil Admolene (a catalyzed linseed oil)	Saturated and/or unsaturated: Aliphatic fatty acids Aldehydes Aliphatic Esters Paraffins Olefins	Harsh, pungent odor characteristic of short chain aldehydes (cause eye watering to varying degrees)
3 Dark Linseed Oil 580°F.	Raw Linseed Oil	Saturated and/or unsaturated: Carboxylic acids Aliphatic esters Alkyl aldehydes Paraffins Olefins Unsaturated: Acids Esters Aldehydes	
0-Pale linseed oil 580°F.	Alkali refined linseed oil	Saturated and/or unsaturated: Aliphatic fatty acids Olefins	
1-Pale linseed oil	Alkali refined linseed oil	Saturated and/or unsaturated: Fatty acids Saturated Aldehydes Olefins	
00-Pale linseed oil	Alkali refined linseed oil	Saturated and/or unsaturated: Aliphatic carboxylic acids Unsaturated alkane esters Saturated alkyl aldehydes Olefins	
Tall oil alkyd 475°F.	Tall oil Glycerine Fumaric acid	Saturated and/or unsaturated: Carboxylic acids Esters Aldehydes Alcohols Paraffns Olefins Fumaric acid	Hydrogen Sulfide (Rotten egg odor)
Tall Oil Alkyd 560°F.	Tall Oil Glycerine Pentaerythritol		Very offensive —Hydrogen Sulfide, n-butyl mercaptan (skunk odor)
Soybean oil alkyd 475°F.	Soybean oil Glycerine Fumaric acid Rosin	Saturated and/or unsaturated: Aliphatic carboxylic acids Aliphatic alcohols Alkyl aldehydes Alkane esters Paraffins Olefins	Mild soapy & slightly lemon-like odor
Linseed oil alkyd 475°F.	Alkali refined linseed oil Glycerine Phthalic anhydride Litharge	Aromatic acids Aromatic esters Aromatic aldehydes Aliphatic Carboxylic acids Aliphatic Aldehydes Aliphatic alcohols	Typical linseed oil cooking odors (harsh and stinging)

Table 2. Odor and composition (by functional groups) of oil and varnish fumes.

in extremely dilute concentrations. Many such compounds have noticeable odors in concentrations of one part per million and less (Table 3).

Mixing and Thinning Processes

The addition of solvents and thinners to oils, resins, varnishes and lacquers may be an important source of air pollution where large quantities of highly volatile materials are involved. Many processes require the addition and mixing of solvents during the cooking process, in which case the amount of solvent lost to the atmosphere will be governed by its volatility, the temperature of the material to which it is added, the degree of mixing, and the extent of additional heating, if any.

Thinning of premixed paint pastes to the consistency required by the user involves dilution with aliphatic or aromatic hydrocarbons, alcohols, ketones, esters and other materials which are highly volatile at normal temperatures. Although some plants use open vat mixing with certain solvents, the volatility of most thinners requires that mixing be done in totally enclosed tanks to prevent appreciable losses of these expensive products. In general, the loss of solvents to atmosphere from such mixing amounts to no more than 1 or 2% of the solvent used.

The addition of powdered solids for mixing or reaction with paint and varnish vehicles can be a source of atmospheric dust pollution unless such materials are properly handled. Pulverized pigments may be carried through the exhaust system and discharged to the atmosphere if suitable controls are not used. The batch addition of other powdered materials such as phthalic anhydride to cooking kettles may produce a dust discharge of several minutes' duration even with a scrubber on the vent system.

Miscellaneous Sources

While the principal atmospheric pollution from a vehicle manufacturing plant results from the venting of cooking and mixing vats, there may be other minor sources of pollution within the plant, the importance of which will depend on the raw materials used, plant location, type of air pollution created and the seriousness of other sources. Factors such as spillage, leakage, or loss from vaporization of stored materials may make a greater contribution than casual observation would indicate. Each problem will require evaluation and solution on the basis of all the factors involved. An example of the extent to which control may be required is the case

Bodying oils	Running natural gums	Manufacturing oleoresinous varnish	Manufacturing alkyd varnish
Water vapor	Water vapor	Water vapor	Water vapor
Fatty acids	Fatty acids	Fatty acids	Fatty acids
Glycerine	Terpenes	Glycerine	Glycerine
Acrolein	Terpene oils	Acrolein	Phthalic anhydride
Aldehydes	Tar	Phenols	Carbon dioxide
Ketones		Aldehydes	
Carbon dioxide		Ketones	
		Terpene oils	
		Terpenes	
		Carbon dioxide	

Table 1. Composition of oil and varnish fumes.

Losses to atmosphere will vary depending on composition of ingredients, rate of temperature application, maximum temperature attained, method of introducing additives, degree of stirring, type and extent of air or inert gas blowing, and length of time kettle is held at maximum temperature. Maximum losses normally occur during the high temperature cycle of the cook. Total loss of oleoresinous varnish cooks may average to 6% with some losses reported as high as 10-12%. Losses from the production of alkyd resins may range from 4-6%. Cooking and blowing of oils may produce from to 3% loss, while heat polymerization of acrylic resins may run less than 1%, unless the reaction gets out of control and overflows the kettle.

Most modern plants employing high temperature processes use closed kettles vented through a duct system to a central discharge point. Some smaller plants still use open kettles, but these are usually hooded and vented through a duck system.

The composition of fume constituents given off during heat processing of the four major classes of oils and varnishes as listed by J. J. Mattiello (16) is shown in Table 1. Using infrared spectrometer techniques, C. W. Selheimer, et al (12) (13), identified the functional groups present in the fumes from several high temperature polymerization and esterification processes (Table 2).

In the heat bodying of natural oils, saturated and unsaturated aldehydic substances are among the decomposition products produced. The harsh, pungent odors of short chain aldehydes are typical byproducts of this as well as other cooking processes involving such oils. In addition to their objectionable odor properties, unsaturated aldehydes cause eye watering and nose and throat irritation. Acrolein (or acrylic aldehyde) which was used as a tear gas in World War I, is an unsaturated aldehyde commonly identified with oil cooking processes and is readily recognized by its disagreeable odor and irritating qualities. This is a decomposition product of glycerine which may have been included in the reactant as an additive or produced by breakdown of the oil during heating. Unsaturated aldehydes, acids and esters are likewise produced in varying degrees during the manufacture of oleoresinous varnishes and alkyd resins. The decomposition and reaction products of various additives to any process make their own distinctive contributions to the escaping fumes.

In the tall oil glycerine pentaerythritol esterification process, small quantities of sulfur in the tall oil are responsible for the creation of highly offensive odors in the fumes produced. Hydrogen sulfide is given off during the heating up period and n-butyl mercaptan (skunk odor) is produced during the high temperature cycle. The hydrogen sulfide odor from this process becomes more pronounced as the temperature of the cook is increased. Some suppliers are now refining tall oil in an effort to remove as much of the sulfur as possible before it is used in vehicle production.

It is of interest to note that both tall oil and pentaerythritol contain only carbon, hydrogen and oxygen (with a small amount of sulfur in the tall oil); however, the degradation or oxidation products comprising the fumes from the esterification of these materials might contain several thousand compounds including aldehydes, ketones, hydrocarbons, the sulfur compounds mentioned, and various organic acids such as ordinary saturated and unsaturated hydroxy, aldehydic, dicarbonylic and ketonic acids. The sulfur compounds, like a number of other malodorous components which create the primary air pollution problem from cooking processes, occur in concentrations which ordinarily cannot be detected by wet chemistry, infrared or mass spectrometry techniques, but are readily detected by the human nose.

The development of water emulsion and water soluble coatings in recent years has resulted in additional raw materials being used for making vehicles, and, as might be expected, this has brought about an increase in atmospheric odor problems. For example, in manufacturing latex coatings involving the polymerization of certain acrylic monomers such as methyl methacrylate, the monomer itself is highly volatile and has a strong sickening sweet odor. Control of the vapors from this raw material during storage and handling must be as complete as the control of fumes produced during polymerization.

Many of the odor problems resulting from the manufacture of paint and varnish vehicles are made exceedingly difficult because the malodorous compounds involved have very low odor thresholds and thereby create objectionable odor conditions even though they exist

Material	Concentration ppm.	Odor
olein	1.8	Acrid odor
maldehyde	0.062	Eye and nose irritant
etaldehyde	0.066	Eye and nose irritant
ethyl methacrylate	1.0	Sickening sweet
butyl mercaptan	0.001	Skunk odor
drogen sulfide	0.13	Foul (rotten eggs)
yl sulfide	0.00014	Garlic odor
lfur Dioxide	1.0	Pungent

Table 3. Odor threshold concentrations.

a plant using large quantities methyl methacrylate: it is ated in a semi-residential area and was at one time subjected to erous complaints. After evaling every possible source of or, this plant has been forced to t special precautions at all es of storage and handling, now considers the spillage of pint of the raw monomer a us offense. Every precaution taken against spillage and valve age. Special leak-proof contors are used on the hose when ying the tank truck into the rage tank. The saturated vapor hausted from the raw monomer rage tank is vented through vated charcoal to prevent its pe to the atmosphere each time tank is filled. Additional vated charcoal adsorbers are ed over the tank truck man- opening and over the vent charging from the monomer ing room. Special instructions ere furnished the supplier to inre delivery of the raw material in tank truck free from odor and th all valves tightly closed against slightest leakage.

ontrolling Atmospheric Emissions

On the basis of experience gained ough trial and error, several rly good methods for the disal of fumes from cooking operations have been developed. They re:

1. Condensation and absorption by scrubbing with water.
2. Condensation and absorption by scrubbing with alkali or acid washes.
3. Combustion.
4. Dispersal from high stacks.

No one control method has proved suitable for all applications. Many control devices now being used are, at best, only partially effective.

Fumes from cooking processes are composed of a heterogeneous mixture of gases, vapors, and particulates (both liquid and solid). Any one of these types of contaminants, by itself, might be effectively controlled by a single appropriate method. However, such a mixed composition does not lend itself well to highly effective control by any single method other than combustion. Although comparatively high fume removal efficiencies may be obtained with scrubbers in terms of the total mass of fumes collected, the bulk of material removed, may be innocuous water and easily condensed vapors, while those components having particularly objectionable odors may pass through the control device with much lower efficiency of removal.

A pilot plant study will often be worthwhile in determining the most effective and economical method of fume control for a given process, and may save costly or grossly inefficient installations. Considerable practical information regarding the composition and character of fumes from any process may be obtained by collecting samples with the apparatus described by Selheimer, et al (4) (5) (13), employing an air cooled condenser, a water condenser, a water or other liquid scrubber, dry ice-acetone condenser and activated carbon adsorption unit (Fig. 1).

Pilot plant studies will not predict every condition which will arise with the full scale unit. Allowance should be made for this possibility. An example of this is a catalytic combustion unit installed to operate at 750° F. Although the initial objectionable odor of the fumes was destroyed at this temperature, a secondary objectionable odor developed during combustion. A temperature of 950° F. in the catalytic unit was required to eliminate this secondary odor.