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AP42 Section 7.1

Related: 14

Title: Review of Hydrocarbon Emissions Related to Coal

Tar Pitch. Includes pitch vapor pressure data and Antoine's coefficients.

EF Bart, et al. Allied Chemical Corporation 1980

REVIEW OF HYDROCARBON EMISSIONS

RELATED TO COAL TAR PITCH

E. F. Bart, S. A. Visnic, P. A. Cerria

Allied Chemical Corporation
Morristown, New Jersey 07960

Summary

Coal tar pitch is used primarily as a binder in the manufacture of carbon electrodes for the aluminum and steel industries. The pitch represents the main product from the continuous, high-temperature distillation of coke oven tar. The pitch is produced and generally handled as a liquid at high temperatures, thus resulting in a potential for hydrocarbon emissions during its handling.

An ever-increasing need for control of hydrocarbon emissions has resulted for process and storage equipment since amendments were made in 1977 to the Clean Air Act. Within the next several years, most industries will be faced with requirements for the installation of air pollution control equipment. This paper deals with the types of emissions and methods used in quantifying and controlling emissions from coal tar pitch storage equipment. To better understand the nature of coal tar pitch, a brief description is given of its origin, chemistry and physical properties.

Coal Tar Distillation

Coal tar pitch is the residue from the distillation of coal tar and represents from 30% to 60% of the tar. It is a complex, bituminous substance and has been estimated to contain about 5,000 compounds. Of these, less than 130 have been isolated and identified.

The present-day process for fractionating coal tar primarily used in industry is continuous distillation. The first step is the removal of water from the coal tar. When coal tar is received, it contains from 3% to 10% water. This water is generally removed by pumping the coal tar from a storage tank through a series of heat exchangers to increase the temperature from about 175°F to about 400°F. The primary heat source is supplied by the oil and pitch products leaving the distillation process. A steam heater, or small furnace, is used to provide any secondary heat required. The 400°F tar enters a fractionating column-vapor box arrangement in which the water and light oil are vaporized. The vapors exit the top of the distillation column and pass through a condensing system. The light oil-water mixture is separated as a result of the difference in their specific gravities. Some of the light oil is refluxed back to the column in order to control the top of column temperature. The water, which is contaminated with phenolic

and ammonia compounds, is fed to a water treatment facility. The dry tar that exits the vapor box is called dehydrated tar and contains approximately 0.1% water or less.

The second step in the process involves heating the dry tar to a temperature of 600°F to 650°F in a furnace to remove approximately 20% of the lighter boiling fractions (one and two-ring compounds) present in the coal tar. This portion of the distillate is often called chemical oil, and contains low-boiling tar acids and naphthalene. This hot tar enters a fractionating column that may be operating at reduced pressure. The general purpose of the column is to separate the vapors that flash into two or three fractions that are further processed to produce high-purity naphthalene, tar acids, and creosote oil components. The vapors are condensed with a portion of the condensate being refluxed in order to maintain the top of column temperatures as desired. The tar leaving this operation is called topped tar.

The third step is removing another distillate which contains approximately 30% of the higher boiling fractions (three, four, and five-ring compounds). The product is called creosote oil. Primary components are acenaphthene, carbazole, fluorene, phenanthrene, pyrene, anthracene, fluoranthrene, chrysene and picene. The topped tar enters a fractionating column-vapor box arrangement where the vapors are separated into two or three components. As in the other two steps, condensing and reflux are used to maintain desired temperatures. Most coal tar distillers have the capability to operate at reduced pressures in this step. The distillation results in the production of light creosote oils, heavy creosote oils, and coal tar pitch. Figure 1 recaps the flow of materials in a typical coal tar distillation unit.

Physical Properties and the Chemical Structure

The chemical composition and also the physical properties of pitch depend on several factors. Among these factors are the nature of the coking process from which the tar is derived, the nature of the distillation process by which the pitch is separated, and whether the final pitch is a blend of pitches, or a direct product.

All pitches are brownish-black or black in color and have a "tarry" odor, probably due to trace quantities of naphthalene and phenol not removed during the distillation process. The pitches can range from viscous liquids at room temperature to materials which are brittle solids.

The only fractions of pitch from which pure chemical compounds can be isolated and analyzed are the distillate oils. The compounds positively identified consist mainly of polynuclear aromatic hydrocarbons or heterocyclic compounds containing three to six rings. The part of coal tar pitch which is sufficiently volatile to distill, appears to be made up of the same oils which are present in crude tar, but are partly removed in converting tar into pitch. The major isolated compounds progress, as the boiling range is increased, from single ring benzene, thiophene, and pyridine derivatives to those containing one six and one five-membered ring (indene, indole), then to the naphthalene and quinoline series, and finally to three-membered ring systems (anthracene, phenanthrene as shown in 1966 in Hoiberg (4)). It is because of the complexity of this heterogenous mixture that coal tar pitch is so difficult to completely collect and analyze.

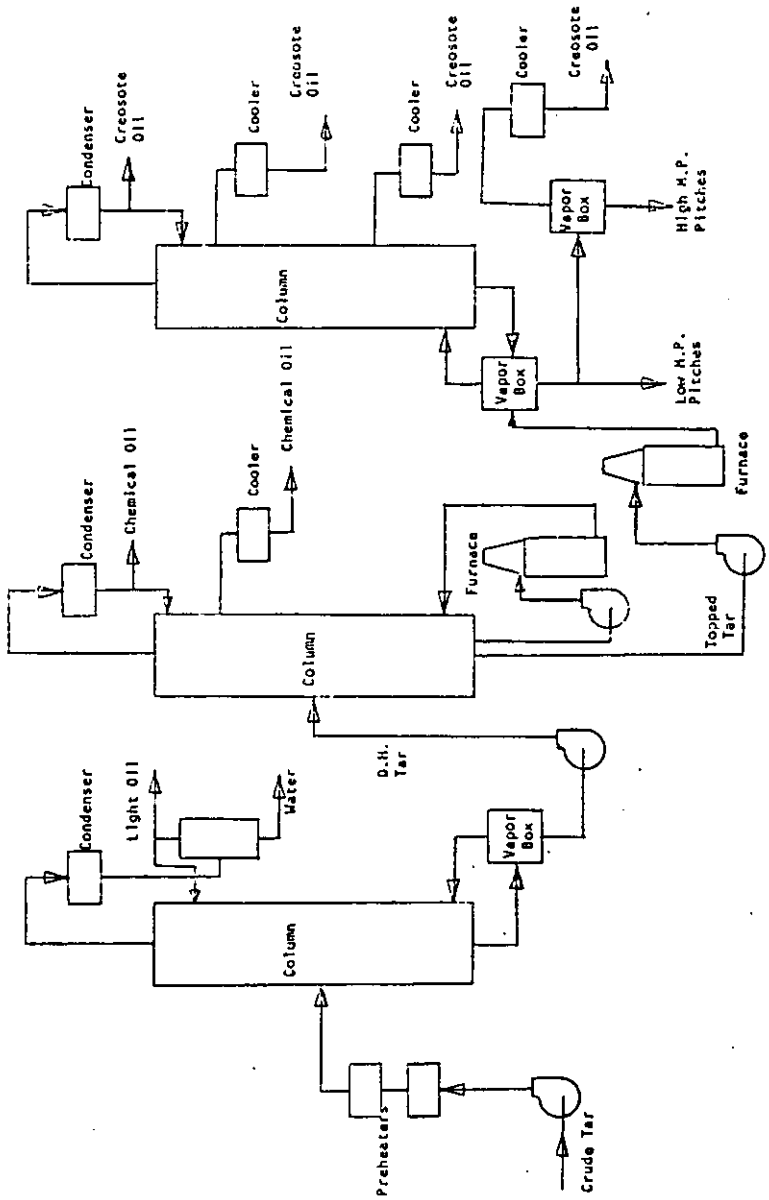

Figure 1. Flow of Materials in a Typical Coal Tar Distillation Unit

Types of Emissions from Storage Tanks

The physical properties and chemical composition of coal tar pitch dictate that it normally be stored in fixed roof storage tanks rather than floating roof tanks. Because of its high softening point and the tendency for its vapors to condense and crystallize, a floating roof storage tank is not recommended for fear of fouling of the seal and hence immobilization of the tank roof. We will, therefore, concentrate only on emissions from the storage of coal tar pitch in fixed roof tanks.

Hydrocarbon emissions, or evaporation losses, occur when evaporated hydrocarbons escape to the atmosphere. Evaporation losses from fixed roof tanks may be divided into two categories; breathing loss and working loss. Breathing loss is associated with thermal expansion and contraction of the vapor space resulting from the daily temperature cycle. They include vapors expelled because of the thermal expansion of existing vapors, and/or expansion caused by barometric pressure changes, and/or an increase in the amount of vapors from added vaporization in the absence of liquid level change, except that which results from boiling as shown in 1976 by Burklin and Honerkamp (3).

Working loss is associated with a change of liquid level in the tank, which may include both the displacement of vapor by a rising liquid surface and the outbreath of vapor following a rapid withdrawal. For most liquid materials, the filling loss occurs when the liquid transferred into the storage tank displaces an equal volume of air, saturated or nearly saturated with hydrocarbons, and vents the air to the atmosphere. However, coal tar pitch, because of its high temperature, also has working losses from the expansion of the vapor space due to an increase in temperature caused by the hot, incoming pitch. This initial expansion of the vapor space results in the following:

(1) The initial rapid air expansion causes high emission volume until the air is displaced.

(2) The air contacting the initial pitch vapors produces condensation and creates an aerosol.

Because of this mixture of air, aerosol and pitch vapor, and the large increase in vapor volume, control of pitch emissions becomes a different and difficult control problem.

Estimation of Emissions

Mathematical Methods

Several methods exist for the quantification of emissions from storage tanks. The most widely accepted method for estimation of emissions from fixed roof storage tanks is the API method (1) for breathing losses and working losses. The equation for estimation of breathing losses is:

$$Ly = \frac{24}{1000}\left(\frac{P}{14.7-P}\right) 0.68\ D^{1.73}\ H^{0.51}\ T^{0.50} F_P C$$

Where:

Ly = breathing loss (bbls/yr)

P = true vapor pressure at bulk liquid temperature (psia)

D = tank diameter (ft)

H = average outage, including correction for roof volume (ft)

T = average daily ambient temperature change (^{o}F)

Fp = paint factor

C = adjustment factor for small diameter tanks

The preceding equation is generally applicable for gasoline storage tanks. For correcting the losses for other materials, the following correction is generally used by the API:

$$Lb = \left(\frac{0.08\ M}{W}\right) Ly$$

Where:

Lb = breathing loss (bbls/yr)

M = molecular weight of vapor (lb/lb mole)

W = condensed liquid density of vapor (lb/gal)

When density data for the condensed vapors cannot be obtained, the original breathing loss equation can be used for coal tar pitch and other materials by using the density of the stored liquid. The equation becomes:

$$Ly = \rho\left(\frac{P}{14.7-P}\right)\ 0.68\ D^{1.73}\ H^{0.51}\ T^{0.50}\ Fp\ C$$

Where:

Ly = breathing loss (lb/yr)

ρ = density of stored liquid (lb/gal)

The API equation (2) for estimating working losses is:

$$F = \frac{2.25\ PV\ Kt}{10{,}000}$$

Where:

F = working loss (bbls)

P = true vapor pressure at bulk liquid temperature (psi)

V = volume of liquid pumped into tank (bbls)

Kt = turnover factor

The same equation is used to calculate the working losses for tanks containing other liquids by adjusting it with the 0.08 M/W term.

Once again, should density data for the condensed vapors be inaccessible, the equation can be used with the liquid density to yield:

$$F = \rho \frac{2.25\ PV\ Kt}{10,000}$$

Where:

F = working loss (lb/yr)

ρ = density of stored liquid (lb/gal)

V = volume of liquid pumped into tank (gal/yr)

Recently, further studies in 1978 by Wilson (7) have been conducted on the estimation of working losses. The studies have evolved around the two basic assumptions of the API equation:

(1) The vapor space in the tank is saturated.

(2) Every barrel of oil pumped into the tank displaces 5.61 cubic feet of vapor.

From field studies, Wilson found that both assumptions are incorrect the majority of the time. For storage tank operations, the amount of vapor forced out of the tank should only be calculated by the total upward movement of the liquid level, since in many cases, the liquid is pumped out at the same time it is pumped into the tank.

The studies by Wilson also showed that the average vapor concentration in storage tanks was 66% of the theoretical saturated vapor concentration. Using the 66% saturation and the total upward movement of the liquid level, the working loss equation becomes:

$$E = (1.2 \times 10^{-4})\ PVM$$

Where:

E = emissions (lbs)

P = true vapor pressure at bulk liquid temperature (psia)

M = molecular weight of vapors (lb/lb mole)

V = volume of displaced vapors (scf)

In the preceding breathing and working loss equations, the vapor pressure for liquid pitch is used. The curve for 110°C softening point pitch is shown in Figure 2 as developed in 1969 (6).

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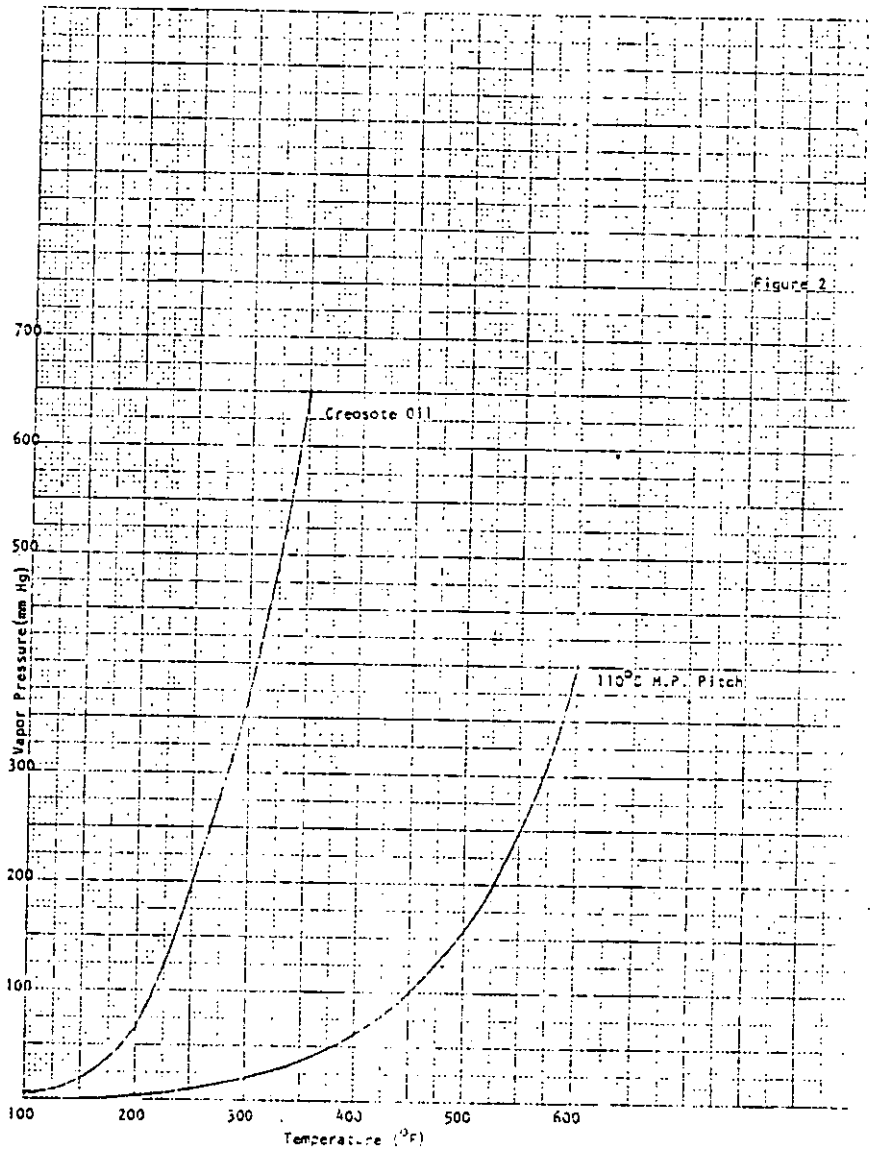

Figure 2. Curve for 110°C Softening Point Pitch as developed in 1969

Another method for estimation of working losses which has been used on coal tar pitch storage tanks is a model based on the expansion of the vapor space when hot pitch is pumped into the tank as shown in 1975 by Hooker (5). Since pitch is pumped to storage tanks at temperatures anywhere from 300°F to 750°F, the expansion of the vapor space and corresponding vapor emission is much greater than breathing losses or working losses due to the displacement of the vapors. This model, therefore, becomes useful for obtaining the maximum emission rate when first pumping hot pitch into a relatively colder storage tank. The method assumes that the inlet to the tank is a submerged fill pipe used to reduce contact between the incoming pitch and the air space.

The volume of pitch vapor given off over a short interval, say one minute, of time when pumping into a tank is estimated as follows:

$$E = \frac{F}{7.48} + \left[\left(\frac{\Delta ts}{ts + 460}\right)\left(\frac{Vt - Vp}{7.48}\right)\right]$$

Where:

E = vapor emissions (cubic feet)

F = inlet pitch flow (gpm)

t_s = vapor space temperature at start of interval (°F)

Δt_s = change in vapor space temperature during the interval (°F)

Vt = tank capacity (gal)

Vp = volume of pitch in tank at start of interval (gal)

Simplifying the above equation gives:

$$E = 0.134 \left[F + \left(\frac{\Delta ts}{ts + 460}\right)(Vt - Vp)\right]$$

The change in the vapor space temperature is expressed as follows:

$$\Delta ts = \frac{1}{60}\left[\frac{Ap\ Up\ (tp - ts) - Aw\ Uw\ (ts - ta)}{WsH}\right]$$

Where:

U = heat transfer coefficient $\left(\frac{BTU}{hr.\ ft^2\ {}^oF}\right)$

A = heat transfer area (square ft.)

t = temperature (°F)

W = weight of vapors (lbs)

H = heat capacity of vapor $\left(\frac{BTU}{lb\ {}^oF}\right)$

sub a = ambient

sub p = pitch surface

sub s = vapor space in tank

sub w = uninsulated wall and roof surface

Typical values for U and H used for coal tar pitch calculations are 1.5 and 0.25 respectively.

The equation for calculating W_s is:

$$Ws = 0.0763 \left(\frac{520}{ts + 460}\right) \left(\frac{Vt - Vp}{7.48}\right)$$

Combining the last two expressions and dropping the term $\frac{520}{ts + 460}$ as an unnecessary refinement, gives the simplified equation for calculating the change in vapor space temperature (Δts):

$$\Delta ts = 9.8 \left[\frac{Ap\ (tp - ts) - Aw\ (ts - ta)}{Vt - Vp}\right]$$

Using no larger than one minute time intervals over a given time, the total vapor flow and the weighted average vapor temperature can be determined. By using the total vapor flow, the weighted average vapor temperature, and the field-measured final vent temperature, the amount of pitch (oil) vapors emitted can be determined by the following expression:

$$Wo = \Sigma_o^m E \left(\frac{520}{tsa + 460}\right)\left(1 - \frac{P}{760}\right)\left(\frac{P_2}{760 - P_2}\right)\left(\frac{M}{379}\right)$$

Where:

Wo = amount of pitch (oil) vapor discharged (lbs)

tsa = weighted average vapor temperature (^oF)

P_1 = oil vapor pressure at weighted average vapor temperature (mm Hg)

P_2 = oil vapor pressure at weighted average final vent temperature (mm Hg)

M = molecular weight of oil vapors (lb/lb mole) = 160

If a very short tank vent exists, the tank vapor temperature essentially equals the final vent temperature and the equation becomes:

$$Wo = \Sigma_o^m E \left(\frac{520}{tsa + 460}\right) \left(\frac{P}{760}\right) \left(\frac{M}{379}\right)$$

Since the above emission calculation is based on the vapor volume emitted, the vapor pressure data utilized is for coal tar creosote oil which is actually the material emitted from coal tar pitch. A vapor pressure curve for creosote oil is also shown in Figure 2.

Sampling and Analytical Methods

Many methods have been used for determining hydrocarbon emissions from coal tar pitch and other liquid storage tanks. One widely-used method is the collection of vapors in an evacuated bottle. The vapors are then analyzed using a gas chromatograph equipped with a flame ionization detector (FID). Using the vapor concentration and the tank vent vapor rate, the actual mass rate of emissions is obtained.

In order to obtain a more representative sample, a longer sampling time is required. This can be accomplished by using a sampling train and portable vacuum pump to condense and collect the vapors in a known solvent or solvents. A typical sampling train is shown in Figure 3. Since coal tar pitch is comprised of mostly "heavier" hydrocarbons, hexane can be used as a solvent although consideration of solvent loss during the sampling period is important. After sample collection in the solvent, the sample is analyzed using a gas chromatograph with a FID. The collected sample can be further analyzed using a mass spectrometer to distinguish individual compounds. However, this is not required if only the mass emission rate is necessary. Gas flow rates from a tank vent are generally measured using a pitot tube.

Another method which is becoming more and more popular is the use of a portable hydrocarbon vapor analyzer. The unit gives a direct readout of hydrocarbon concentration (in ppm) and when interfaced with a recorder will show the different peaks in a chromatogram.

As a result of the ease and speed of these analyzers, many samples can be taken to give an accurate picture of the vapor constituents. It is because of the great flexibility of these units that their use has become increasingly popular, as shown by the EPA's field use. Their use could possibly become the approved method for determining hydrocarbon emissions.

Control Equipment

Condensing equipment, ejector-venturi scrubbers and electrostatic precipitators are the more common methods for controlling hydrocarbon emissions from coal tar pitch storage facilities. Several types of condensing systems can be utilized. Waterbox condensers consist of cooling coils submerged in a water bath. The temperature of the water should be kept above 175°F to prevent the possible plugging of the coil by the crystallization of naphthalene and other compounds.

Shell-and-tube condensers can also be used to reduce pitch emissions. Once again, tempered water must be employed to prevent the plugging of the condenser. The shell-and-tube condenser is more susceptible to plugging, but is used because of the higher efficiency and lower space requirements. Because of their smaller size, the shell-and-tube condenser can be conveniently located on top of the storage tank.

Air-cooled condensers are used where tempered water systems are impractical. Air-cooled condensers for coal tar pitch vapors actually have large diameter vent piping arranged in a coil-like pattern. They use the ambient air to condense the pitch vapors. These condensers are less efficient than water-cooled condensers, but are advantageous because they are less susceptible to plugging and do not need a water system.

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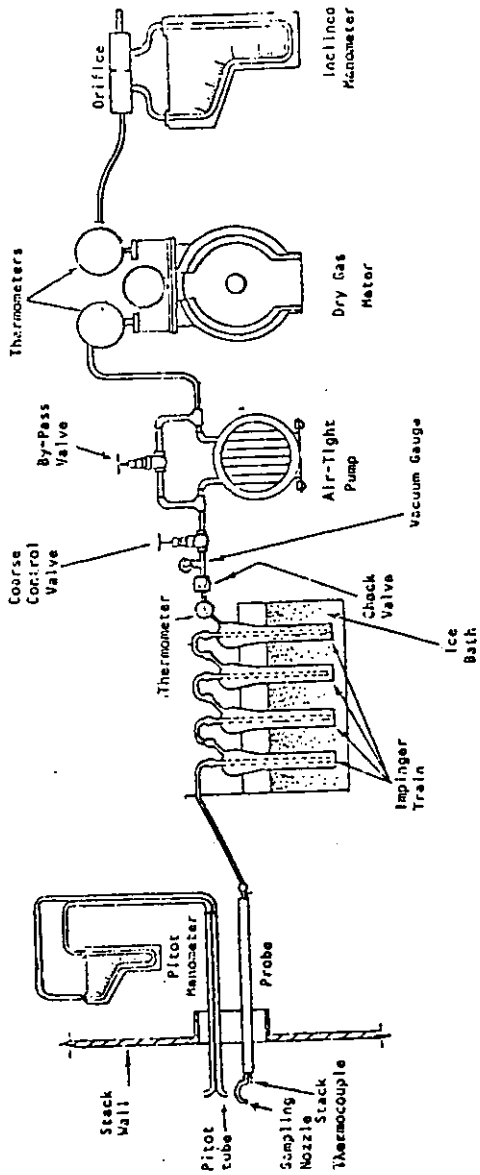

Figure 3. Typical Sampling Train

Ejector-venturi scrubbers have seen much use for controlling emissions from pitch tanks. This scrubber works on the same principle as a steam ejector; a high velocity spray creates a slight draft or vacuum and draws the vapors into the scrubber where the vapors are thoroughly mixed and scrubbed by a scrubbing liquid. The scrubbers are more practical when a high boiling coal tar solvent can be used as the scrubbing liquid, rather than water. By using a coal tar solvent, the scrubber performance is increased since the solvent gives improved scrubbing and condensing effects because of the solvent's compatibility with the pitch vapors. By eliminating the use of water as the scrubbing liquid, the need for treating the scrubber waste water is also eliminated.

Small scrubbing units can be operated for each tank or a large, centrally located scrubber can be used on several tanks. For units operating on API atmospheric storage tanks, special precautions must be taken when the unit is operated under a no-load or small vapor flow condition. The unit can develop increased vacuum when the pitch vapor rate decreases substantially. This condition exists after the tank vapor space has expanded due to the high pitch temperatures. Once the vapor space temperature has stabilized, the vapor emission rate is greatly reduced and a vacuum increase will result from the scrubber. Extreme care must, therefore, be taken to eliminate the possibility of a vacuum increase which could result in the collapse of the storage tank.

One of the newer methods of controlling pitch emissions is with low-voltage electrostatic precipitators. Because of the intimate contact between the air in the tank and the incoming hot pitch, pitch vapor emissions initially consist primarily of an aerosol. An electrostatic precipitator removes the liquid aerosol droplets very effectively by electrically charging the liquid particles and later collecting the charged particles on oppositely charged collecting plates.

The major drawback of the electrostatic precipitator in pitch service is the maintenance required to clean the collecting plates. Since the collected particles are a semi-liquid rather than either liquid or solid, it is very difficult to incorporate a self-cleaning system into the unit. Therefore, most electrostatic precipitators are used on batch installations where time is available to manually clean the unit.

In addition to the control equipment previously mentioned, several methods exist which will give minor reductions in pitch emissions. The methods are relatively inexpensive and, depending on the allowable emission rate, may be satisfactory. They include the use of breather valves and submerged fill pipes.

Breather valves, or conservation vents, allow a slight pressure and vacuum on the tank to reduce or eliminate the normal breathing losses. Breather valves will not generally handle the working losses, unless a high pressure setting is used; but care must be taken so the pressure setting does not exceed the tank's pressure rating. In addition, the breather valves must be cleaned periodically to prevent buildup of semi-liquid materials.

Submerged fill pipes are utilized on many installations. They reduce the contact between the incoming pitch and the air/vapor mixture already in the tank, by introducing the material into the bottom of the tank. By reducing the contact between liquid and vapor, there is less vapor space expansion and less aerosol formation.

Although the submerged fill pipes do not greatly reduce emissions, they do find use in conjunction with other control equipment. The dip legs greatly enhance the capabilities of condensing and scrubbing equipment by reducing the vapor load and quantity of aerosol sent to the control equipment.

The exact control equipment or combination of control equipment is dependent on many factors. Therefore, details of tank operations and requirements of air agencies should be thoroughly researched before control equipment is selected.

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Pitch vapor pressure data

F	psi	logpsi	C
150	0.019342	-1.713496	65.55556
200	0.096711	-1.014526	93.33333
250	0.193421	-0.713496	121.1111
300	0.386842	-0.412466	148.8889
350	0.676974	-0.169428	176.6667
400	1.160526	0.064655	204.4444
450	1.934211	0.286504	232.2222
500	3.094737	0.490624	260
550	4.835526	0.684444	287.7778
600	7.736842	0.888564	315.5556

Antoine's Constants

$A = 3.354727$

$B = 1286.645$

$C = 192.6373$

$$\log P = A - \frac{B}{T_c + C}$$

Based on Figure 2 in Review of Hydrocarbon Emissions Related to Coal Tar Pitch