

Better understanding needed for asphalt tank-explosion hazards

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Basic differences in the generation of combustible gas vapors in tanks storing four classes of asphalt materials.

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ments.

It has been clearly shown that classical methods of thinking about and troubleshooting these hazards only work for flux and paving asphalts (and can break down even for these materials), and are not applicable to solvent deasphalted residuum and air-blown asphalts.

The latter have been shown, for the first time, to pose a special problem due to their continued reactivity after undergoing the air-blowing process. Time and temperature are critical parameters in determining and controlling the degree of this problem.

Simple measurement techniques were developed to monitor all these hazards, and these techniques are considered to be necessary to more accurately determine the vapor space hazard in all asphalt tanks.

Background. In spite of the extensive use of hot asphalt for over a century, little has been published on the nature of explosion hazards in its storage tanks. Most of what has been

published has emphasized that the flash point of the material stored is the most important factor in determining if enough fuel is present in the vapor space for combustion.¹⁻³

Dimpfl⁴ concluded that factors unrelated to simple evaporation of asphalt are common causes of the build-up of combustibles in asphalt tanks. He cited smoldering coke deposits on the inner roof and shell of the tank

(SDA) processes, contamination from crude feed/vacuum residuum heat exchanger leaks, and unstripped light hydrocarbons generated during air blowing as being potential sources of vapor space fuel not detected by flash point tests.

He emphasized smoldering coke's role in depleting oxygen and elevating carbon monoxide and carbon dioxide in the tank vapor space, and pointed out its potential as an ignition source, with or without the catalyzing effect of iron sulfide. However, based on his sampling of nine tank vapor spaces, Dimpfl was not able to predict what material and storage conditions tended to give explosive vapor spaces. His final conclusion was that the storage of asphalt is an unpredictable art.

The work described in this article was undertaken to build an understanding of the factors affecting the accumulation of combustible vapors in tanks storing various types of asphalt. The key to this effort has been an extensive tank vapor space-mon-

itoring program in which we have developed simple methods of evaluating asphalt tank vapor-space compositions.

The methods are currently being used in our manufacturing facilities to define specific tank hazards, thus providing us with an ever-expanding data base to aid in predicting and controlling high-risk situations. This in-plant testing is being complemented by lab

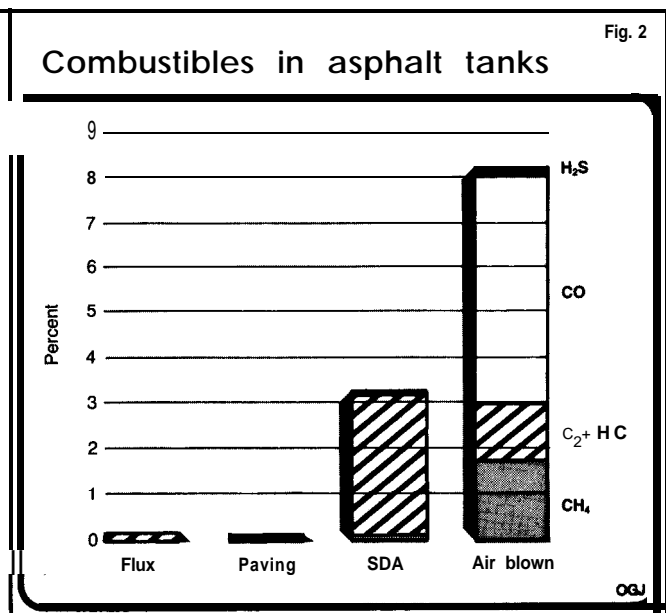
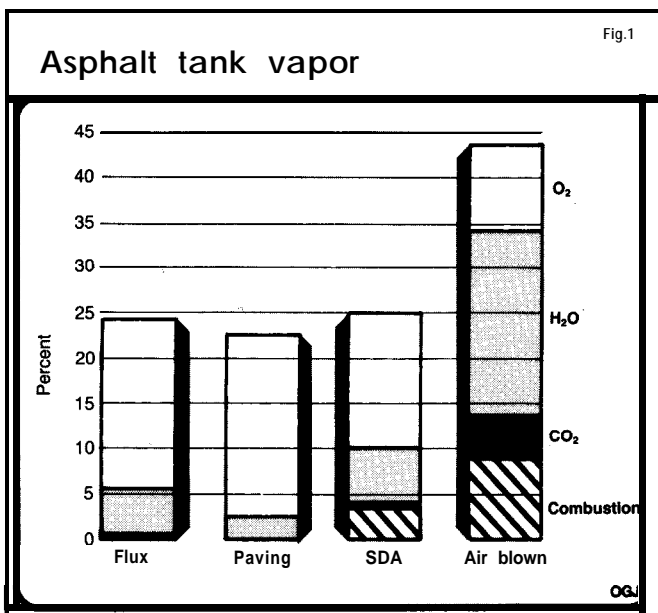
sophisticated characterization of actual vapor spaces.

A verification of the accuracy of the simpler tank-monitoring methods has been completed, and that work is being prepared for publication.

Vapor-space compositions. To date, our measurements of nearly 2,000 individual vapor spaces in over 200 tanks has led to the view of asphalt tank vapor-space compositions summarized in Figs. 1, 2, and 3.

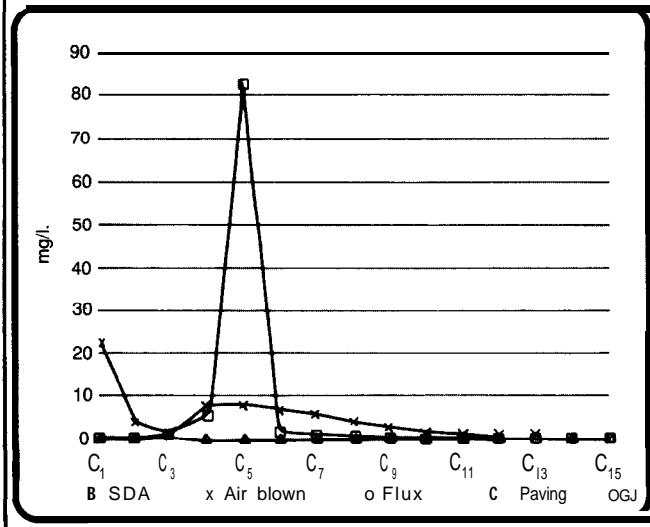
All three figures present data on four classes of hot asphalt tanks—those storing roofer's flux (vacuum tower bottoms generally of low viscosity and high flash point that can be processed into high softening point grades of roofing asphalt by air blowing), paving asphalt, SDA, and air-blown asphalts. Included are examples of vapor-space compositions.

In the case of the flux and paving asphalt tanks, the values presented represent overwhelmingly typical values. The SDA and air-blown asphalt tank values reflected hazardous ex-



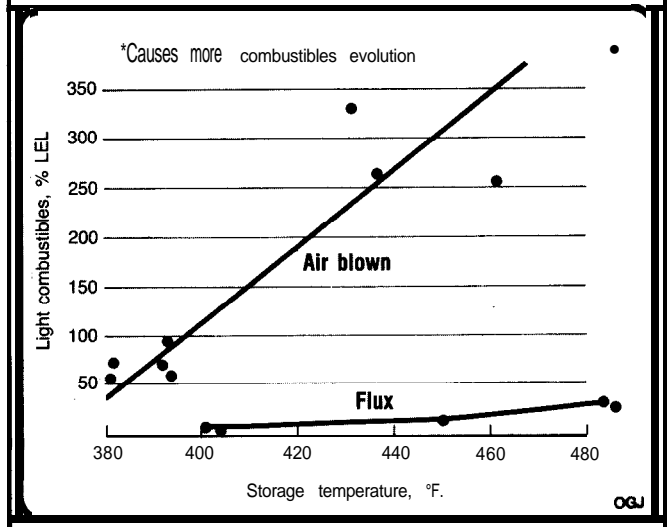
Hydrocarbons in tank vapor space

Fig. 3



Air-blown asphalt*

Fig. 4



tremes that, while far from typical, were encountered often enough to be of general concern.

At the other extreme, the vapor spaces in tanks storing these two materials look very much like the vapor spaces in the flux and paving tanks. The vapor space of an SDA tank was generally at one of these two extremes, while in air blown asphalt tanks both extremes and all points in between are common.

Fig. 1 divides the example tank vapor space compositions into four components: combustibles, carbon dioxide, water vapor, and oxygen, and presents them in a stacked bar chart. The difference between the total bar height and 100% is nitrogen from air. Note that none of the tanks discussed in this study were inerted.

From the data, it is clear that typical flux and paving tanks have little more than nitrogen, oxygen, a little water vapor, and a very small amount of combustibles in their vapor spaces, the SDA residuum tanks had, in the extreme case, a large combustible gas fraction, and again in the extreme case, the air-blown asphalt tanks had a large combustible gas fraction as well as large water vapor and carbon dioxide levels.

Fig. 2 divides the important combustible gas fraction into four additional levels: methane, other hydrocarbons, carbon monoxide, and hydrogen sulfide. The data on our examples, once again, indicate nothing hazardous in the typical flux and paving tanks and only the "other hydrocarbon" fraction in the SDA tank.

The extreme air-blown asphalt tanks, on the other hand, had large methane and carbon monoxide combustible fractions in addition to a large "other hydrocarbon" fraction, and

was the only tank example to have a significant amount of hydrogen sulfide in the vapor space.

Finally, Fig. 3 breaks the "other hydrocarbon" fraction of Fig. 2 into a profile of carbon number molecules. These data indicate that the flux, paving, and air-blown asphalt tanks had a broad spectrum of hydrocarbons present in their vapor spaces, whereas the SDA tank had a single spike at the carbon number that in every case of high combustible gas readings in our experience corresponded to the solvent used in producing this material.

The data summarized in the above examples give a view of hot asphalt tanks as follows.

Combustible gas buildup in flux and paving tanks can typically be characterized by their flash points. Since these materials are generally stored at temperatures substantially below their COC flash point, the vapor spaces are typically low in combustible gas levels.

Flux and paving tanks thus tend to follow the traditional view of asphalt tank safety as being well-defined by flash point measurements. Contamination problems with these materials are not unknown but not commonly encountered.

When contamination does occur, the control of hazards by flash point can break down, depending on the contaminant and the flash point method generally used. We have monitored over 100 tanks storing these materials and have only seen elevated combustible gas levels with flux stored at high temperatures where the flux was inadvertently aerated, and with paving that was made from blending solvent contaminated SDA material.

Solvent deasphalted residuum can

create a tank vapor space problem because of solvent contamination from the deasphalting process if the steam stripping of the material is not adequate. This problem appears to be a strong function of the supplier's process, the solvent used, and the amount of ventilation in the tank where the material is stored.

Because of the high volatility of the solvents in question (propane through pentane), these hazards are not detected by flash-point tests.

Finally, from the data in Figs. 1 and 2, it is obvious that air-blown asphalt is an entirely different material from a tank-hazard standpoint, and it deserves some more extensive discussion. The basic uniqueness of this material from a loss-prevention standpoint has not, to our knowledge, been recognized before.

Again, the high levels of volatile combustibles, like methane and carbon monoxide, make flash-point testing inadequate.

Air-blown asphalts. An experiment done in Trumbull's pilot plant convertor illustrates the basic difference in the air-blown asphalt hazard. Roofer's flux was loaded into the convertor (1,000-gal capacity) and stored at a specified temperature overnight.

The heating medium in all these tests was hot oil circulating through a heat exchanger countercurrent to the asphalt flow. The system was such that the hot oil was never more than 25° F. hotter than the target asphalt storage temperature.

The vapor space in the convertor was sampled in the morning for very light combustibles. This sampling, which will be discussed later, used an activated charcoal tube to adsorb hydrocarbons of carbon number three and higher so that only very light-end

combustibles were measured.

The flux was then air blown to one of a variety of endpoints ranging from 160°F. to 230° F. ring and ball softening point (the softening point of the original flux was about 90°F.), and was again stored overnight at a certain temperature. The same measurement of light combustibles was performed on the tank vapors the next morning.

Fig. 4 presents results from many of these experiments. The data show a dramatic difference in behavior between air-blown asphalt and the flux from which it was blown.

As expected, the flux does not evolve significant light-end combustibles even at temperatures approaching 500° F., hence the measured values are low and the slope of the combustible gas composition vs. storage temperature is small. With the air blown material, the light combustible gas values are orders of magnitude higher, and the dependence on temperature is dramatic.

Two possibilities exist to explain this difference. First, as suggested by Dimpfl, light combustibles formed during air blowing may be entrained in the asphalt, and may evolve after the blowing is over.

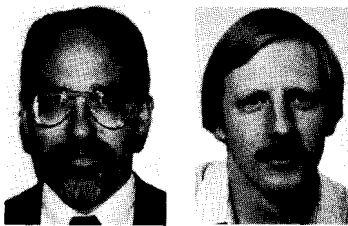
This explanation was discounted because the high combustible gas values occurred even when the material was extensively steam stripped during and after air blowing, and light combustible gas evolution was highly dependent on temperature, even with the same material stored for successive nights at different temperatures—a simple evolution of entrained gases would not have exhibited this tendency.

The second explanation, which we accept, is that the reactions occurring in the air-blowing process result in a newly blown material which is far more reactive and more susceptible to thermal cracking. This reaction mechanism explains the high temperature dependence of the combustible gas buildup, the ineffectiveness of steam stripping, and the nature of the gases in the vapor space as illustrated by the high concentrations of light combustibles in Fig. 4 and the high levels of methane, carbon monoxide, hydrogen sulfide, and carbon dioxide shown to be present in Figs. 1 and 2.

Others^{5,6} have shown that these four compounds are the gaseous products most readily formed by thermal cracking at lower temperatures in asphaltene-pyrolysis studies. The potential for thermal cracking of newly air-blown asphalt has also been observed in our routine monitoring of the asphalt tank-vapor spaces.

From these data, it is apparent that the reactivity of the material dissipates

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with time. For example, in cases where the material is pumped from the converter to one storage tank then transferred to a second tank, the first tank invariably has higher combustible gas levels than the second, even if both are held at equal temperatures.

It is also apparent that, as shown in Fig. 4, the level of thermal cracking leading to high combustible gas levels is strongly affected by material temperature. For example, tanks storing blown asphalt to be poured into cartons are nearly always very low in combustible gas readings because the asphalt has been cooled to below 400°F.

Finally, the presence of very hot surfaces in contact with the asphalt, e.g., a hot firetube heating unit operating in an unagitated tank or with a heavy coke buildup, has been observed to be a contributor to high combustible gas levels because of an increase in thermal cracking. Obviously, knowledge of these factors can be used to control the hazard in air-blown asphalt tanks.

The first step toward this control is the monitoring mentioned throughout this article which identifies the tanks that need a process change to reduce combustible gas levels.

A condition mentioned prominently in Dimpfl's paper, but not considered in the preceding discussion, is the buildup of light-hydrocarbon combustible gases, carbon monoxide, and carbon dioxide as a result of smoldering coke deposits on the inner roof

and shell of the tank. This phenomenon could lead to some of the observations discussed in this article, but has been ruled out as a frequent mechanism because of the relatively high oxygen content in most vapor spaces, and our knowledge concerning the cleanliness of some of the problem tanks.

It is obviously not a factor in the data of Fig. 4 because the smoldering coke deposits would also have influenced the flux data, and because the pilot converter was known to be deposit free. It is, however, still important to recognize this risk.

It is also important to realize that not only will newly blown asphalt thermally crack more readily, but it will also react with oxygen more readily. This can occur in thin films on clean walls or over existing coke deposits. This can lead to buildup of a potentially dangerous coke problem.

It can also occur if the asphalt is pumped into the vapor space of a tank instead of being added below the liquid level. In extreme cases, the latter situation can create vapor compositions which are similar to those expected with smoldering coke deposits.

Tank-monitoring methods. To do the routine vapor-space monitoring mentioned, we use the following equipment:

1. A combination combustible gas and oxygen meter that reads out in percent LEL from 0 to 100 and percent oxygen from 21 down to 0. To accurately measure the combustibility of the many and varied chemical species present in an asphalt tank, the meter should operate by catalytically burning the vapors and sensing the change in resistance of the heated wire as a result of this combustion.

In our studies, we used Mine Safety Appliance Models 261 and 360 explosion meters. Other manufacturers offer instruments using a similar measurement technique.

These meters are designed to be portable, and are made primarily for testing empty tanks to assure safe conditions prior to tank entry. They are therefore, often already available in an asphalt facility.

2. A small activated carbon tube of the sort commonly used to take hydrocarbon samples. To get the first breakdown of combustibles into their component parts, we placed these tubes in-line between the tank and the combustion meter.

With the meter thus configured, the hydrocarbons above a carbon number of two are adsorbed on the activated carbon, and only the very light combustibles are passed through and measured by the combustion meter. As a

practical matter, this reading is an indication of the amount of methane and carbon monoxide being generated and can be used to determine if a high combustible gas reading is due to solvent contamination or the reactions of thermal cracking or oxidation.

For example, in the case of a very high combustible gas reading in a tank storing solvent-deasphalted residuum, if that reading were reduced to near zero by inserting the carbon tube prior to the meter, then solvent contamination would be the strongly suspected cause of the combustible gas in the vapor space.

However, a high reading with the carbon tube in place would indicate thermal cracking as the cause of the high combustibles.

3. Gas indicator tubes. The tubes are the size of small pencils, and are used with a simple hand pump pulling approximately 100 ml through the tube in a single stroke.

Vapor concentration is indicated by the change in color of the media in the tube. These tubes are used to measure carbon monoxide and carbon dioxide as a followup to determine if a smoldering-coke problem exists. A low oxygen reading is the first indicator of this problem.

Gas-indicator tubes can also be used to measure hydrogen sulfide, a potential ignition hazard because of its tendency to react with iron oxide to form iron sulfide which will catalyze the auto-oxidation of coke and is, itself, a potential pyrophor.^{7 8}

In asphalt tanks, hydrogen sulfide in the vapor space is also evidence of thermal cracking. With these simple and easily applied measurements, an asphalt tank vapor space can be analyzed to an extent sufficient to approximate the stacked bar charts illustrated by Figs. 1 and 2.

The hydrocarbon profile in Fig. 3 was prepared by depositing vapor samples on charcoal tubes and by taking gas-bomb samples. Both samples are analyzed with a gas chromatograph with an infrared detector.

The data given in this article should not be construed as recommending changes in practices that have been successful in avoiding asphalt-tank explosions. All manufacturing operations are different, and the safety procedures that work in one are not necessarily directly transferable to another.

It is hoped, however, that the clearer view of asphalt tank safety presented in this article will lead to better engineering practice with asphalt tanks and fewer explosions in asphalt plants.

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