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EMISSION OF AIR POLLUTANTS FROM THE PROCESS OF WASTE VARNISH INCINERATION

The objective of our study was to investigate what kinds of pollutants are emitted into the atmosphere in the course of waste varnish incineration and how the process parameters affect the formation of the pollutants released. It was found that the incineration of oil paints produced predominantly aldehydes and smaller amounts of aromatic hydrocarbons, whereas that of phthalic resins generated mainly alcohols. The distribution of pollutant concentration during the incineration cycle was also investigated. Hence, after 10 minutes of oil paint incineration only slight concentration of air pollutants was measured. However, during ashing of phthalic resins their concentrations measured after 30 minutes were still high.

Air pollutants formed in the course of waste paint or varnish incineration have to be degraded, best of all by catalytic or thermal oxidation. Also the method for the disposal of ashes produced in this process depends on the composition of the wastes being incinerated (different metals, also harmful or toxic heavy metals used as pigments or fillers).

1. INTRODUCTION

In the past few years, the problem of municipal and industrial waste management has become more urgent in Poland. Wastes from paint processes constitute a considerable portion of the total industrial wastes. They include mixtures of solvents, waste paints or varnishes collected in a variety of tanks or floating in the form of skins or emulsions. In developed countries, wastes of that type are disposed of by high- or low-temperature incineration. To make the process friendly to the environment it is necessary to choose an appropriate incinerator and to determine the optimum process parameters (temperature, air flow velocity, duration of the process, etc.). Such incinerators are not manufactured in Poland.

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Flue gases from the low-temperature (ca. 400 °C) pyrolysis of waste paints or varnishes contain a number of air pollutants, both gaseous and solid. Along with the major products of incineration (i.e., CO₂, H₂O, CO, etc.), the process generates also hydrocarbons and their oxy-derivatives (aldehydes, alcohols, ketones, esters). When the incinerated wastes include chlorine-laden plastics or paints, the emissions from the combustion process may carry highly toxic polychlorinated dioxines and difuranes, present in the gaseous phase or condensed on the fly ash. Organic gaseous air pollutants can be removed by catalytic or thermal combustion, whereas particulates are eliminated in cyclones or electrostatic precipitators. The fly ash, as well as the solid wastes produced in the course of the low-temperature varnish pyrolysis, containing different metals (also harmful or toxic heavy metals) have to be disposed of on the special landfills. Thermal utilization is the only method of disposal for this type of wastes [1]–[3]. It was therefore interesting to determine not only the minimum time required for the incineration of typical paints, but also the qualitative and quantitative distribution of the pyrolysis products in the course of the process.

The objective of the study was:

to identify and quantify the air pollutants generated during low-temperature pyrolysis of the most common varnish wastes,

to determine how the process parameters (time of the process and air flow velocity) affect the formation of air pollutants.

2. EXPERIMENTAL

The experiments were run with three types of samples comprising typical wastes collected at the Paint and Varnish Manufacturing Plant POLIFARB S.A., Wrocław.

Sample A comprised spent general-purpose oil paints consisting of phthalic binders, painter's naphtha, fillers (manganese, cobalt and lead compounds) and pigments (ferrite-chrome yellow, zinc white and other zinc compounds).

Sample B contained phthalic resin wastes with the following components: phthalic resins, modified melamine-formaldehyde resins, solvents, zinc white and titanium oxide.

Sample C included polyacetate resins containing polyacetates, solvents and sodium hydroxide.

Sample A came from the rubbing process, whereas sample B and sample C were collected at the resin synthesis department.

The laboratory setup for waste incineration is shown in figure 1. The horizontal quartz reactor (6) with a ceramic sampling boat (9) was heated in an electric furnace (2). Temperature was measured by a thermocouple (5) connected to a recorder (4). Process temperature was controlled by autotransformer (3). Air was fed through an air pump (1); flow velocity was controlled with a valve (11) and measured with a rotameter (10).

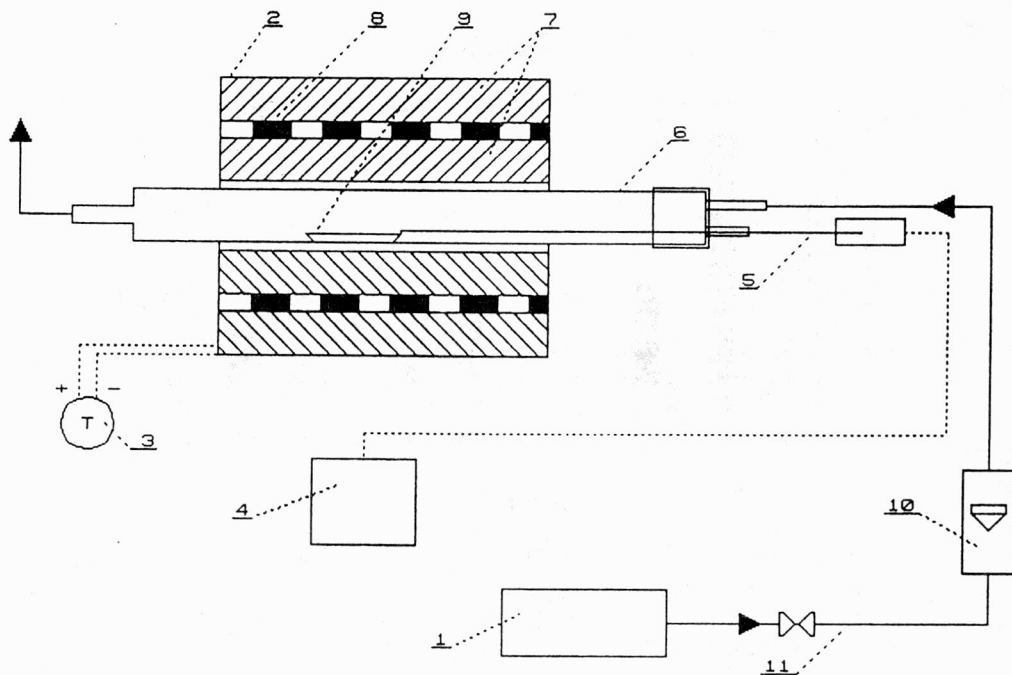


Fig. 1. Laboratory setup for waste incineration

1 - air pump, 2 - furnace, 3 - auto-transformer, 4 - temperature recorder, 5 - thermocouple, 6 - quartz reactor, 7 - thermal insulation, 8 - electric heater, 9 - ceramic sampling boat, 10 - rotameter, 11 - control valve

The experiments were run at the following parameters:

weighed portion of the waste, about 1 g;

air flow velocity, 20, 40 and 60 dm³/h;

time of sampling: at the beginning of the process, after 10 minutes and after 30 minutes;

temperature of the process, 420 °C (this value was determined in an earlier test reaction and is equivalent to the minimum pyrolysis temperature for the ashing of the three investigated wastes).

3. RESULTS AND DISCUSSION

Low-temperature pyrolysis of each sample produced solid residues in the form of ash. The weight of each sample was reduced to ca. 20% of its initial value.

Analysis of organic air pollutants, both qualitative (in terms of retention time) and quantitative, was carried out by gas chromatography using a Hewlett-Packard GC 5890 Series II apparatus equipped with flame ionization detector (FID) and a HP-1 capillary column (Fused Silica Capillary Column, 30 m × 0.53 mm × 2.65 μm). Gas samples for analysis were injected with a gas syringe.

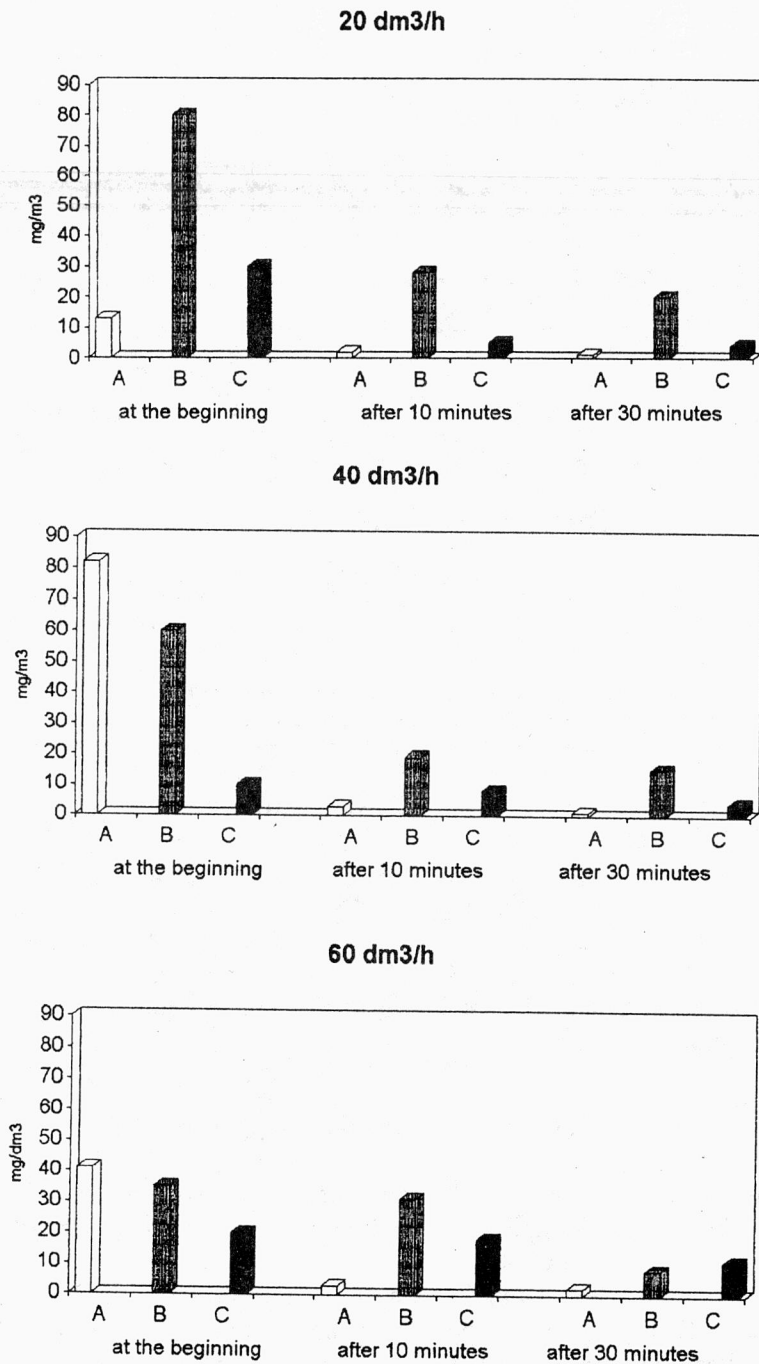


Fig. 2. Total concentration of organic air pollutants emitted versus time of incineration at different space velocity

The total concentrations of air pollutants from low-temperature pyrolysis of the samples A, B and C were related to the duration of the process and to the air flow velocity. The plots are presented in figure 2. As shown by these data, the concentration of organic pollutants decreased with the duration of the process irrespective of the type of the waste being incinerated, but the value of the pollutant concentration depended noticeably on the type of the sample. Thus, after 30 minutes of incineration, the concentration of total organic compounds in the sample A dropped to 1.3–3.2% of the initial value, whereas those in the sample B and sample C to 20–28% and about 52% of the initial values, respectively. Also air flow velocity influenced the total concentration of air pollutants. Thus, for the sample A, the highest initial concentration, 82.3 mg/dm³, was observed at the air flow velocity of 40 dm³/h. For the sample B and sample C, the highest initial concentrations, i.e., 81.2 and 28.4 mg/dm³, respectively, were observed at the lowest air flow velocity which reached 20 dm³/h.

Qualitative analysis of organic air pollutants allowed us to detect the presence of aliphatic and aromatic hydrocarbons, aldehydes, alcohols, ketones and esters as well as small amounts of organic acids in each sample investigated. Of the aliphatic hydrocarbons present in the flue gas, methane occurred in the highest concentration; the concentrations of pentane, *n*-heptane, octane or nonane being much lower. This finding holds for each of the waste samples tested. The aromatic hydrocarbon concentration varied according to the type of the incinerated waste. During low-temperature pyrolysis of the sample A and sample C the highest concentration was that of benzene, whereas in the sample B xylene concentration was found to be the highest. Of the oxy-derivatives during ashing of the sample A, the dominant part played such compounds as methanol, propionaldehyde, methyl ethyl ketone and ethyl acetate. The concentration of oxy-derivatives during pyrolysis of the sample B and sample C as well as the proportion of every compound group in the total pollutants concentration varied slightly according to the velocity of air flow through the reactor. In the group of alcohols, the contribution of methanol to total concentration decreased, and that of butanol increased with the increase in air flow velocity. For sample B the lowest air velocity generated the highest concentrations of isovaleric aldehyde, acetone and butyl acetate. The increase in air velocity raised the fractions of acetaldehyde and cyclohexanone in the flue gas. For sample C, the lowest air flow velocity produced the highest concentration of propionaldehyde, acetone and ethyl formate. With the increase in flow velocity, acetaldehyde and butyric aldehyde became dominant among aldehydes, and cyclohexanone among ketones.

Figures 3–5 show the distribution of individual groups of compounds during incineration of the three wastes at the air flow velocity of 40 dm³/h. Gas samples were analyzed at the beginning of the process, after 10 and after 30 minutes.

For sample A (figure 3), the proportion of initially dominating aldehydes decreased from 41% to 24% after 30 minutes. There was also a decrease in the

concentration of aliphatic hydrocarbons the proportion of which dropped from 11 to 4%. The proportion of aromatic hydrocarbon concentration increased from 27 to 37%, and that of alcohols from 1 to 19%. The concentrations of the remaining groups and their variation were insignificant.

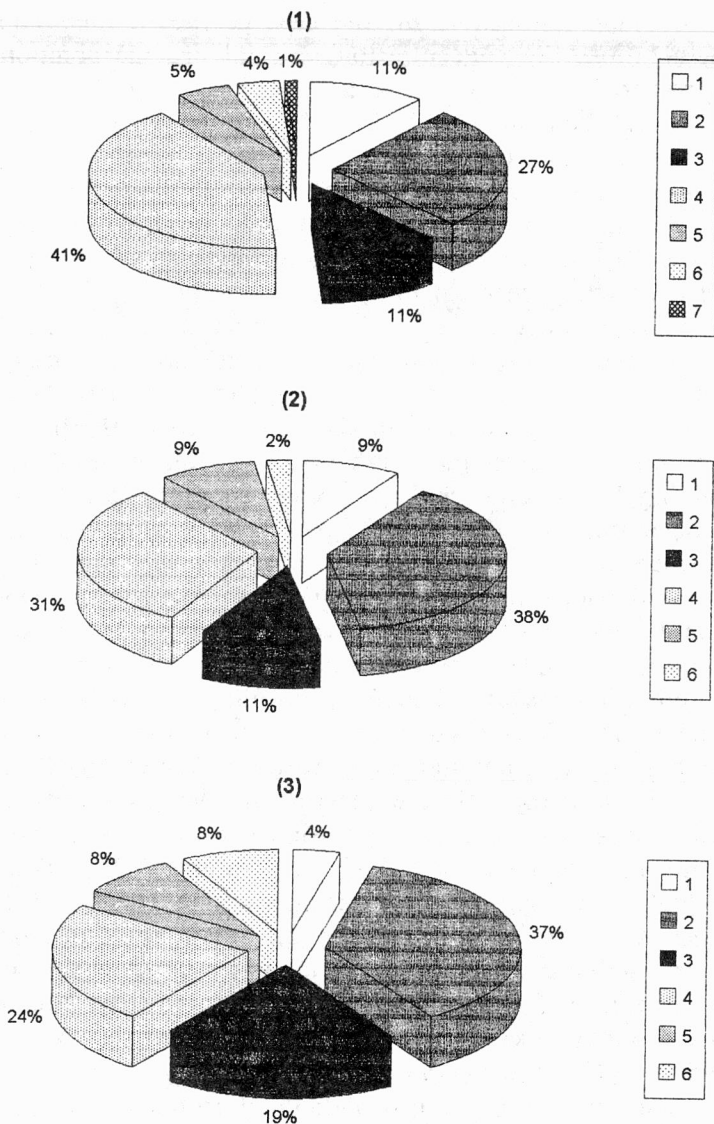


Fig. 3. Distribution of concentrations in particular groups of pollutants in flue gas during incineration of sample A
 flow velocity, 40 dm³/h; (1) at the beginning of the process, (2) after 10 minutes, (3) after 30 minutes
 1 - aliphatic hydrocarbons, 2 - aromatic hydrocarbons, 3 - alcohols,
 4 - aldehydes, 5 - ketones, 6 - esters, 7 - organic acids

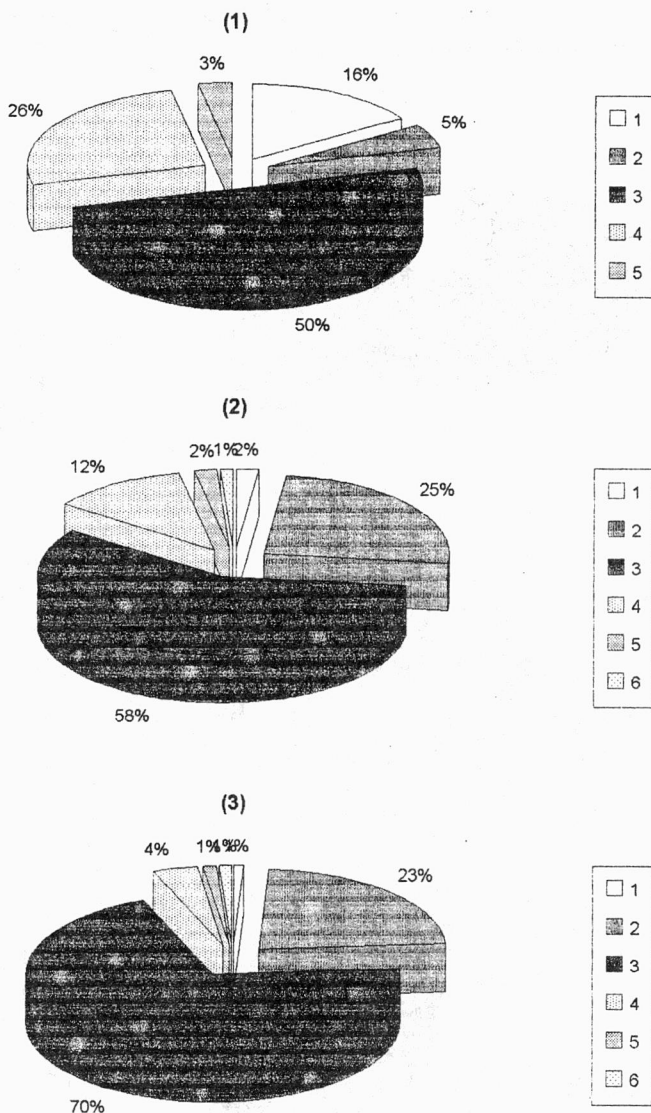


Fig. 4. Distribution of concentrations in particular groups of pollutants in flue gas during incineration of sample B

flow velocity, 40 dm³/h; (1) at the beginning of the process, (2) after 10 minutes, (3) after 30 minutes

1 – aliphatic hydrocarbons, 2 – aromatic hydrocarbons, 3 – alcohols, 4 – aldehydes, 5 – ketones, 6 – organic acids

For sample B (figure 4), the concentration of alcohols was dominant, and their proportion rose from the initial value of 50% to 70% after 30 minutes. A similar pattern was observed for the behaviour of aromatic hydrocarbons; their fractions increased from the initial value of 5% at the beginning of the process to 23% after

30 minutes. At the same time the fractions of aldehydes dropped from 26 to 4% and that of aliphatic hydrocarbons from 16 to 1%.

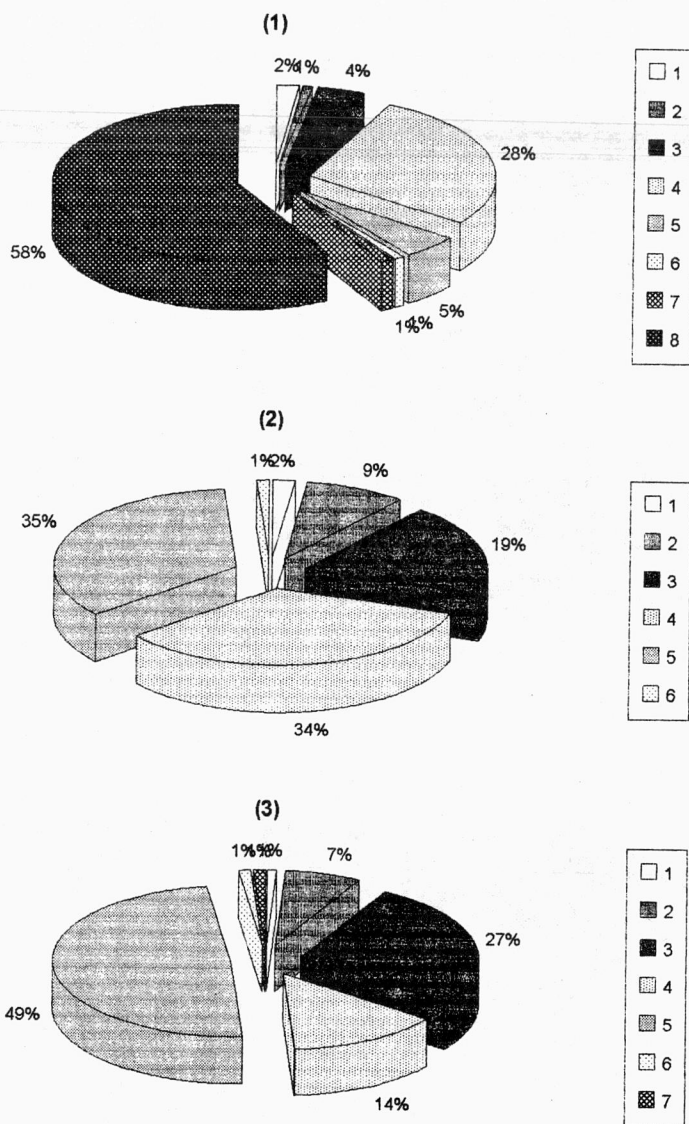


Fig. 5. Distribution of concentrations in particular groups of pollutants in flue gas during incineration of sample C
 flow velocity, 40 dm³/h; (1) at the beginning of the process, (2) after 10 minutes, (3) after 30 minutes
 1 - aliphatic hydrocarbons, 2 - aromatic hydrocarbons, 3 - alcohols, 4 - aldehydes,
 5 - ketones, 6 - acetates, 7 - organic acids, 8 - esters

Esters (ethyl formate) were dominant at the initial stage of the sample C incineration (figure 5) with a 58% contribution to total concentration, but within 30 minutes their concentration decreased to zero. Like in the incineration of the sample A and sample B, the proportion of aldehyde concentration decreased (from 29 to 14%), whereas that of aromatic hydrocarbons increased (from 1 to 7%). The concentration of aliphatic hydrocarbons was insignificant and did not vary with time.

4. CONCLUSIONS

On the basis of the results obtained the following conclusions can be drawn:

1. The temperature of 420 °C was sufficient for complete ashing of the three samples investigated. After low-temperature pyrolysis the weight of the ash produced decreased to ca. 20% of the initial weight of the sample.

2. Irrespective of the type of the varnish wastes incinerated, the flue gases contained similar groups of compounds: aromatic and aliphatic hydrocarbons, aldehydes, alcohols, ketones and esters as well as small amounts of organic acids, but the proportion of their concentrations differed from one waste type to another.

3. Air flow velocity had no significant effect on the qualitative composition of the air pollutants produced, but it did affect the total concentration of pollutants; low-temperature pyrolysis of the oil paint sample generated the highest concentration of organic pollutants at the air flow velocity of 40 dm³/h, whereas that of the phthalic resins sample – at the smaller flow velocity of 20 dm³/h.

4. Total concentration of the generated organic air pollutants decreased with the duration of the process, but the rate of the decrease differed from one incinerated waste to another. Thus, in the case of the oil paint sample, the concentration of pollutants dropped to at least one-tenth of the initial value only after 10 minutes, whereas in the case of phthalic and polyacetate resins the concentration decreased to about 25 and 50%, respectively, after 30 minutes.

5. The concentrations of particular groups of pollutants varied in a similar way with the duration of the incineration process. Thus, the concentrations of aromatic hydrocarbons and alcohols increased, whereas these of aldehydes and aliphatic hydrocarbons decreased for all samples investigated.

6. Air pollutants formed in the course of waste paint or varnish incineration have to be removed, best of all by catalytic or thermal combustion. The choice of the method for the disposal of the solid wastes produced depends on the composition of the incinerated paints or varnishes (different metals, also harmful or toxic heavy metals).

ACKNOWLEDGEMENT

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EMISJA ZANIECZYSZCZEŃ POWIETRZA PODCZAS SPALANIA ODPADÓW LAKIERNICZYCH

Celem pracy było określenie składu jakościowego i ilościowego zanieczyszczeń powietrza emitowanych w procesie spalania najczęściej występujących odpadów lakierniczych w zależności od takich parametrów procesu jak: strumień objętości powietrza i czas trwania procesu. Stwierdzono, że spalanie farb olejnych ogólnego zastosowania powoduje emisję przede wszystkim aldehydów, w mniejszym stopniu – węglowodorów aromatycznych. W przypadku żywic ftalowych powstawały głównie alkohole. Również zmiany stężeń w czasie trwania procesu były różne. I tak już po 10 minutach spopielenia farb olejnych stężenia zanieczyszczeń malały niemal do zera, podczas gdy po 30 minutach wypalania żywic ftalowych mierzone stężenia zanieczyszczeń były relatywnie wysokie.

Emitowane zanieczyszczenia powietrza należy unieszkodliwiać, najlepiej metodą spalania termicznego bądź katalicznego. Zagospodarowanie powstałego odpadu stałego – popiołu, uzależnione jest od zawartości w nim metali ciężkich stosowanych do produkcji farb i lakierów jako pigmentów lub wypełniaczy.

ЭМИССИЯ ЗАГРЯЗНЕНИЙ ВОЗДУХА ВО ВРЕМЯ СГОРАНИЯ ЛАКИРОВОЧНЫХ ОТБРОСОВ

Целью настоящей работы было определение качественного и количественного состава загрязнений воздуха, эмитируемых в процессе сгорания наиболее часто выступающих лакировочных отбросов в зависимости от таких параметров процесса, как: струя объема воздуха и время протекания процесса. Было установлено, что сгорание масляных красок общего употребления вызывает эмиссию прежде всего альдегидов, в меньшей степени – ароматических углеводородов. В случае фталевых смол образовались главным образом alkoholi. Также изменения концентраций во время протекания процесса были разными. И так, уже после 10 минут озоливания масляных красок концентрации загрязнений понижались почти к нулю, в то время когда после 30 минут сгорания фталевых смол измеряемые концентрации загрязнений были относительно высокими.

Эмитируемые загрязнения воздуха необходимо обезвреживать, лучше всего методом термического или каталитического сгорания. Использование образованного твердого отброса – золы – зависит от содержания в ней тяжелых металлов, применяемых в лакокрасочных заводах в качестве пигментов или наполнителей.