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RECYCLING POSSIBILITIES FOR THE WASTES RESULTED FROM THE PAINTS AND VARNISHES INDUSTRY BY PYROGENATION

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În acestă lucrare se prezintă o soluție modernă şi viabilă pentru protejarea mediului înconjurător în concordanță cu cerințele şi normele comunității europene pentru reciclarea deşeurilor apărute din industria de lacuri şi vopsele. Lucrarea prezintă o clasificare a acestor deşeuri şi o analiză amănunțită a tipurilor de pigmenți existenti în ele. Se prezintă posibilități de reciclare a acestor deşeuri prin pirogenare şi rezultatele unor determinări experimentale efectuate în acest scop. Pentru anumite situații se recomandă oxidarea totală a reziduului solid. În funcție de tipul deşeurilor utilizate se pot recupera solvenți din produsele volatile, gaze combustibil sau un combustibil solid şi o masă anorganică prelucrabilă în scopuri metalurgice. Se face o estimare a costului investiției reciclării deşeurilor pentru o fabrică de vopsele.

This article presents a modern and viable solution for the protection of the environment in accordance to the requirements and standards of the European Community for the recycling of wastes obtained from the paints and varnishes industry. A classification of these wastes and a detailed examination of the pigments nature are given. Possibilities to recycle these wastes by pyrogenation and the experimental work performed to achieve this goal are presented . For specific situations total oxidation of the solid residue is recommended. According to the used types of wastes it is possible to recover solvents from the volatile products, combustible gases or a solid fuel, as well as an inorganic mass that can be used in metallurgy. An estimation of the investment cost for a paint plant has been given.

Keyword: paints and varnishes wastes, pyrogenation, recycling wastes.

1. Introduction

The development of the paints and varnishes industry in concordance with modern economy requirements is accompanied by important amounts of wastes, which impose modern recycling methods in order to protect the environment.

A possible classification of wastes from paint and varnishes industry is made in two modes: by the waste origin and by the waste characteristics [1].

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2. Classification of wastes by their origin

a. wastes produced during the manufacturing process;
b. wastes found in the finite products deposit;
c. wastes found in the raw materials deposit;
d. wastes from other sources.

a) The wastes produced during the manufacturing could be:

- Hardened layers (shells) resulted from the alkyd paste of the paint pigmentation, appeared both due to the long time storage and insufficient quantity of anti-skinning agent (methyl ethyl cetoxime, acetonoxime);

- Hardened layers (shells) of the products based on the low or fat alkyd resins resulted in the friction process on the ball mill, due to an insufficient quantity of anti-skinning agent (methyl ethyl cetoxime, acetonoxime);

- "Burns" occurred at the paints, caused by very high temperature during the technological process (friction of paints on the three roll mill, inadequately managed);

- Gel products appeared in production of the paints based on aqueous emulsion resins due to the overreach of the recommended pH-intervals, inadequate rheological agents, accidental adds of the ionic surfactants, etc;

- Gel products appeared in the case of the accidental mixing the low with fat resins or in the case of the inadequate use of solvents required for every types of resin;

- Agglomeration of the thickening agent - a consequence of the incorrect pH-intervals during paints processing.

In general, these wastes are useless, but there are some exceptions for the wastes resulted from the production of aqueous varnish and emails. By adjusting the pH interval it is possible to find a future utilization of the materials if the gelling process is not too advanced.

b) Wastes found in the finite products deposit could be :

- Products based on aqueous emulsion resins with coated filling, especially at products with textured appearance but also at coloured paste and product with the resin separated by the filling due to an overtook validity term;

- Products based on aqueous emulsion resins at which a biological contamination appeared, manifested through inadequate smells due to package leakiness, product contamination with fungus, algae etc, insufficient usage of bio-acids or due to the overheating of the fabrication product, which causes the bio-acids evaporation;

- Products based on low or fat alkyd resins with hardened layers formed at surface due to package leakiness of due to an insufficient methyl-ethyl-cetoxine (anti-skin agent);
- Products with an overtook validity term (from residues) with hardened coated filling.

None of these wastes can be used in the manufacturing process.

c) Wastes found in the raw materials deposit could be:

- Gels formed in containers with synthetic resins in aqueous emulsions due to bad packing or incipient polymerization.

d) wastes from other sources could be:

- Damaged and unused packages, made from metal or plastic, from different sources;
- Contaminated bags;
- Solid products (shells) with different origins.

3. Classification of wastes by their characteristics :

- Wastes from aqueous emulsions;
- Wastes from varnish, paints, emails etc. manufactured with different solvents;
- Plastic packing;
- Metallic packing.

In the case of recovering the metals contained in pigment compositions from the wastes in two group we can discus about :

- Wastes with titanium dioxide;
- Wastes with zinc oxide;
- Wastes with iron oxide (yellow, red, blue);
- Wastes with zinc chromate;
- Wastes with organic and carbon black pigments;
- Metallic boxes.

A general characteristic of these wastes is that they are not biodegradable. They contaminate the environment, both by introducing an inert material and through the interaction between atmospheric factors (rains, winds etc.) and wastes components.

Wastes storage, even controlled, implies the accumulation in time of some inert materials, many of them being flammable, with storage areas being blocked and increasing of fire hazards. This problem begins to be one of proportion for any plant, as his production increases.

This paper describes the recycling of the presented wastes by pyrogenation [2, 3, 4].

4. Experimental

The pyrogenation experiments were performed in a two litter metallic flask provided with a sealed cover and a evacuation tube for the resulting gases. The heating took place in an electric furnace with a system of adjusting the temperature at atmospheric pressure, at a temperature gradient of 3 degrees per minute from 20 to 600 degrees centigrade. A stream of air was flown over the resulting solid material formed by pyrogenation to achieve its complete oxidation. Previous experiments established the pyrogenation times according to the nature of the wastes. When this time has been achieved the pyrogenation was stopped, the solid residue was cooled and weighted. In cases where the solvent recovery was not a priority the gases were burned in a flash reactor or evacuated in an air flow.

5. Results and discussions

In the waste recycling industry the main recommendation is the storage of the aqueous emulsion separately from the emulsion based on the organic solvents, with the purpose to recover the organic solvents.

In Table 1 are presented the pigments quantities which exist in a few types of the industrial products (varnishes and paints) then remain like solid residues in the pyrogenation tank. It is justified economically to process separately the wastes in function of the pigments type (zinc and chrome oxide and zinc chromate) if the quantity is bigger than 100 kg per pigment type. The pigments are recovered as a concentrate from the respective metal which could be used further in the metallurgic industry.

Table 2 shows the results obtained by pyrogenation of some wastes from varnishes and paint industry. Pyrogenation process consisted in heating the wastes in the absence of the air in closed metallic retorts. Maximum temperature recommended for this pyrogenation process is of 500 ºC. After the pyrogenation process the results are a solid residue and vapours. The vapours are cooled and transformed in liquids and gases. The obtained solid residue is a non pollutant (consisting in principal of carbon impurified with some metals from pigments). A decrease of the total mass and volume of wastes was noticed during pyrogenation, the mass of the solid residue being around 0,9 – 69 % from the initial mass. The destroying of the plastic packaging of the product was noticed by examining the solid. In entries 1 and 2 the white spirit and in 3 and 4 the toluene were recovered.

Table 1.

Some of the pigments that could be found in industrial products produced in varnishes and paints industry

Products	Pigment quantity, (kg/kg)									
	Titanium dioxide	Yellow organic holcolan	Zinc dioxide	Yellow iron dioxide	Red iron oxide	Zinc chromate	Red organic pigrom	Green chrome	Blue iron.	Carbon black
White alkyd enamel	0.250									
Cream-coloured alkyd enamel	0.200									
Ochre alkyd enamel			0.036	0.170						
Simple red primer					0.100					
Red anti corrosive primer					0.230	0.020				
Red alkyd enamel							0.060			
Brown alkyd enamel					0.210					
Green alkyd enamel			0.050					0.150		
Blue alkyd enamel									0.025	
Grey alkyd enamel	0.150									0.001
Light –green alkyd enamel	0.150							0.020		
Black alkyd enamel										0.050
Yellow alkyd enamel		0.150	0.050							

Table 2.

Products resulted from the pyrogenation of wastes from varnishes and paints industry

Entry	Products	Pyrogenation efficiency of solid residue, (%) **	Solid residue characteristics	Ash of solid residue from pyrogenation, (%)	Ash characteristics	Emission interval for the volatile combustible, (º C)	Maximum emission interval, (º C)
1	Fat alkyd resin (expired)*	23.07	adherent	84.43	Reddish Brown	250 – 510	270 – 430 480 – 500
2	Fat alkyd resin (sample)	24.30	very adherent	89.36	Reddish Brown	335 – 485	345 – 445
3	Alkyd-carbamidic system (expired)*	10.00	poor adherent	44.15	Reddish Brown	370 – 510	450 – 500
4	Low alkyd resin	24.67	poor adherent	68.19	Reddish Brown	340 – 350 415 – 490	430 – 460
5	Vinyl co-polymer in aqueous dispersion (expired)*	86.11	non adherent	69.12	white	370 – 510	490 – 500
6	Polyvinyl alcohol solution (expired)*	3.94	non adherent	24.00	black, under melting point	220 - 455	380 - 420

* expired from the point of view of application time
** calculated in respect with starting material

In the case in which the solvent recovery is not a priority, the resulted volatile products can be processed through a screens system, heated at 800 – 1000 ºC, with the aim of cracking the liquids and obtaining combustible gases with small molecules and hydrogen which can burn and release heat anywhere is necessary inside the plant. When the recovery of the solvent is profitable the pyrogenation reactor should have implemented a cooling installation to condense and separate the combustible liquids and gases.

In the case when the pyrogenation residue cannot be used as fuel, it is recommended, after the pyrogenation processes is finished, meaning the absence of combustible gases, to introduce air in the reactor for the transformation of the organic masses into combustible gas ($CO + N_2$) or in burning gases. In this situation the solid waste quantities remained after the organic material processing are presented in Table no. 3.

Table 3.

Solid residues obtained from the oxidation of the pyrogenated wastes from Table 2.

Entry	Products	Solid residue resulted after the oxidation the pyrogenation residue in respect with, (%)
1	Fat alkyd resin (expired)*	19.40
2	Fat alkyd resin (sample)	21.70
3	Alkyd-carbamidic system (expired)*	4.41
4	Low alkyd resin	17.00
5	Vinyl co-polymer in aqueous dispersion (expired)*	69.51
6	Polyvinyl alcohol solution (expired)*	0.90

*calculated in respect with the amount of initial product

The data presented in Table 3 show a mass decrease between about 1 and 70%, function of the pyrogenated product. The solid residue could enter into the composition of building materials.

Tables 2 and 3 allowed to make an estimation of the number of reactors needed to recover the investigated wastes. For a medium size varnishes and paints plant, the recovering could be done in 3-4 metallic reactors with a capacity of 100 – 150 L, with the diameter of 250 – 300 mm, heated at 500 ºC. The reactors could work discontinuously and could be fitted with a volatile products cooling systems allowing the solvent separation from the combustible pyrogenation gases.

In case of which recovery of the solvent is not a priority, the gases can be passed through a cracking area heated at 800 – 1000 ºC and then introduced into a burning system.

At the emulsion wastes recycling (entries 5 in Table 2-3) the gases can be evacuated in atmosphere after a preliminary mixing with air for cooling and dilution.

During the recovering of large amounts of wastes from metallic packages containing resins, as those from entries 1-4 in Table 3, to the previous recommended recovery plant could be added a supplementary reactor for their melting. This reactor could be made from graphite and heated at 1500 ºC.

For small wastes deposits an array of 3 reactors could processes approximately 300 kg/day into a discontinue system. The heating of the medium frequency currents reactors is expected. An approx. 50 kVA installation can heat one by one all 3 reactors, cracking system and the metal melting reactor.

On the base of the obtained pyrogenation times it was established experimental by that for each reactor it is required a processing time of 3 hours and a cooling time of 5 hours. The electric energy consumption for 3 reactors of 380 V has been estimated to 2 kWh for each kg of waste processed.

A plant with a 2000 t/year paints production has approximately 2% wastes (packing included), meaning 40 t/year or 110 kg/day of wastes. This could lead to an energetic consumption of 220 kWh/day x 0.29 lei/kWh = 63.8 lei/day = 19 Euro/day, for the environment purification without the amortization of the investment.

Taking into account the current prices of reactors that could be used for recycling it results that the cost of the investment raises to 30 000 Euro. If it is skedued to be amortizable in 5 years, it results a cost of 16. 43 Euro/day, which lead to total cost of the recovering of 35. 43 Euro/day. This financial effort is compulsory for a plant from environmental reasons. Otherwise the plant must find other protective solutions which could be more expensive and less efficient.

6. Conclusions

The pyrogenation is an efficient method of the recycling wastes because it eliminates the wastes together with the plastic packaging.

For small quantities of wastes, of approximately 300 – 500 kg per day, the pyrogenation process can be realized in reactors battery heated with medium frequency currents. The reactors could work discontinuously. For a reactor with the diameter between 250 – 300 mm the working time is approximately 3 hours and the cooling time is about 5 hours, the energy consumption per reactor is 50 kVA and 2 kW/kg of wastes. In the case when metallic packings are needed to be melted it is necessary to introduce in the reactors battery a fourth graphite reactor.

When the recovery of the solvent is the main goal, the gases can be burn directly.

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