HAZARDOUS OR NON HAZARDOUS, - A STUDY OF THE CLASSIFICATION OF WASTE ENAMEL SLIPS

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Abstract

Waste classification is an integral part of the waste management. The classification of waste enamel slip makes it possible for the owner to gain a more favourable classification. Storage of the waste can influence the results of the classification. To develop one waste-transforming technology needs consideration to gain "non hazardous waste" classification

Introduction

One stipulation of joining the European Community is that Hungarian companies also meet environmental regulations applied there. Thanks to this the norms applied in Hungary became more strict, to leave directives out of consideration may involve serious consequences. Nowadays it is necessary to deal with environmental protection in Hungary too.

The management of Lampart corporation decided to make order considering the waste enamel slip. The aim was to place the waste enamel slip from pre-privatisation times according to present regulations and waste enamel slip from present production should be treated according to current regulations.

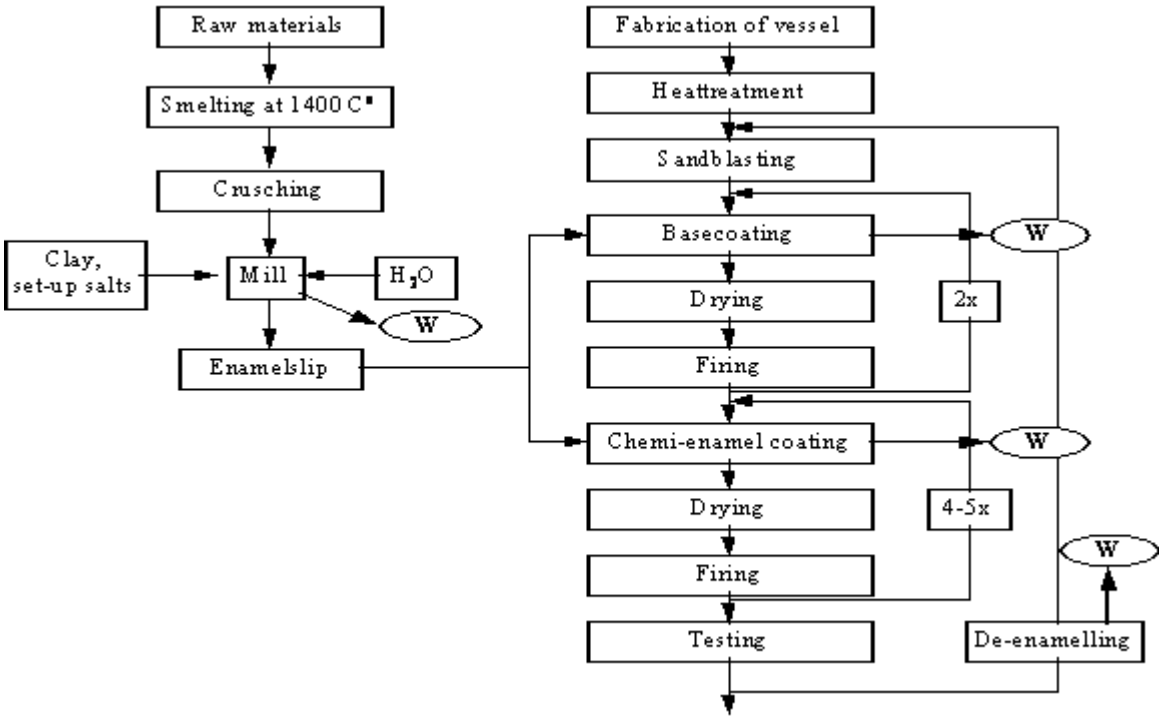
Since the waste enamel slip is included in hazardous waste material list without category classification, it must be considered as "II. hazard class waste" according to its most hazardous component. Waste classification is an integral part of the waste management, because collection, storage, treatment, transport, and possible recycling of the waste material are closely connected with its hazardous classification, respectively the re-classification as "non-hazardous waste". The classification of waste enamel slip makes it possible for the owner, instead of the now automatic second-class classification, to gain a more favourable classification, or in case of favourable test results even get "non-hazardous waste" classification.

We, enamellers, with professional knowledge, hope that waste enamel slip will be classified as non-hazardous waste (except with Cd and Pb content enamels). Therefore we started the classification of our waste enamel slip.

First study

Waste enamel slip from the pre-privatisation times was first chosen for classification. This was half dried slip. Its composition was fine grinded mixture of ground-enamel frit, chemi-enamel frit, clay and set-up salts, and unknown fine grinded ingredients as well. The investigated waste comes from manufacturing, repairing or re-enamelling of enamel coated chemical vessels during the technology is shown in **Figure 1.**

Figure 1.



Steps of the classification

1. Sampling: according to decree 102/1996 (VII.12.) in accordance with norm MSZ 21978/1-86
2. Preparing in accordance with norm MSZ 21978-4
3. Extraction: in accordance with norm MSZ 21978-9
4. Investigation of physical and chemical properties
5. Investigation of the influence of the quantity and the environmental effects of mobile components
6. Ecotoxicological and toxicological investigations
7. Evaluating
8. Proposal
9. Official classification according to the expert's opinion

Test results

Extracts made for investigations were prepared by using the following solvents: distilled water, 4.5-pH acetate-buffer and 2M nitric-acid. The two previous model the effect of live-water and subsoil-water as well as acid-rain and escaped water of communal waste deposits, the later one give an information about the total metal content of the waste.

The given results may be evaluated compared to the concentration limits of drinking-water, sludge and soil.(**Table 1.**)

Table 1.
Hazardous classification according to limit exceeding

	Hazardous classes			
limit exceeding	**Non-hazardous**	**III.class**	**II.class**	**I.class**
compared to sludge limit	0x	>1x	>10x	>100x
compared to agricultural soil limits	0-10x	>10x	>100x	>1000x
compared to drinking-water limits in distilled water extract	0-10x	>10x	>100x	>1000x

compared to drinking-water limits in acetate-buffer extract	0-100x	>100x	>1000x	>10000x

Results of the investigations of physical and chemical properties

Table 2. shows results of original sample investigations in comparison with the relevant limits.

Table 2.

Investigated parameter	Unit		Sludge limit (mg/kg)	Soil limit (mg/kg)	Limit exceeding x (times)
Dry solids content	%	78	-	-	-
Ignition loss	%	2,3	-	-	-
Easily dischargeable cyanides	mg/kg	0,02		0,2	0
Total cyanides	mg/kg	0,08		2	0

There are no reprehensible parameters among the results given from original sample investigations.

Table 3. shows results of investigations of distilled-water extract.

Table 3.

Investigated parameter	Unit		Drinking-water limits (mg/l)	Limit exceeding x (times)
pH		9,5	7,0-8,0	
El.conductivity	mS/cm	523	1350	0
COD	mg/l	29,3	15	2
Nitrite	mg/l	0,50	0,1	5
Nitrate	mg/l	1,1	20	0
Fluoride	mg/l	11,6	1,5	7,7
Chloride	mg/l	43	80	0
Sulphate	mg/l	22	200	0
Sulphide	mg/l	0,5	0,05	10
Ammonia	mg/l	0,57	0,1	5,7
Anionactive det.	mg/l	0,01	0,2	0
Phosphate	mg/l	-	0,26	0

The pH value 9.5 for distilled-water extract can be criticised. There can’t be any objections regarding the other parameters.

Table 4.

	Drinking-water limits (mg/l)	Distilled water extract (mg/l)	Limit exceeding x (times)	Acetate-buffer extract (mg/l)	Limit exceeding x (times)
Aluminium	0,1-0,2	43	**430**	2,3	23
Arsenic	0,05	-	-	-	-
Barium	1,0	1,5	1,5	9,7	9,6
Boron	1,0-5,0	33	**33**	43,3	43
Lead	0,05	-	-	-	-
Cadmium	0,005	-	-	-	-
Chromium total	0,05	2,1	**42**	0,45	9
Chromium VI	0,1-0,5	1,1	**11**	-	-
Cobalt	0,1	1,4	**14**	-	-

Copper	0,2-1,0	0,2	1	0,11	0
Manganese	0,1	0,2	2	0,1	0
Molybdenum	0,07	-	-	-	-
Nickel	0,02	0,7	**35**	-	-
Mercury	0,001	-	-	-	-
Silver	0,01-0,05	-	-	-	-
Thallium	0,01	-	-	-	-
Vanadium	0,05	0,26	5,2	0,1	2
Iron	0,2-0,3	8,6	**43**	0,8	4
Zinc	0,2-1,0	4,3	**21**	0,63	3,2
Tin	0,05	-	-	-	-

COD - Chemical Oxygen Demand

Investigation of influence of the quantity and of the environmental effects of mobile components

Table 4. show results of toxic-metal investigations in distilled-water and acetate-buffer extract in comparison with the relevant limits.

In the case of mobile metals in distilled-water extract the relevant drinking-water limit is exceeded more than ten times by: **B, Cr, Co, Ni, Fe, and Zn**. The **aluminium** exceeds the limit more hundred times. Results of acetate-buffer extract are generally smaller than the results of distilled-water extract and not even one metal quantity exceeds the hundred times value of drinking-water limit indicated as the hazardous category-limit.

The high concentration of aluminium in distilled water extract was fairly surprising. The amount of aluminium-oxide in waste-mixture is on the average 1-2%, according to our recipe, but the total amount does not exceed 4%, which partially get in the system with clay as mill addition.

Table 5. shows results of toxic-metal investigations in 2M nitric-acid extract in comparison with the relevant limits.

Table 5.

Investigated element	**Metal content (mg/kg)**	**Sludge limit (mg/kg)**	**Max. permissible conc. in soil (mg/kg)**	**Limit exceeding x(times)**
Aluminium	7420	-	-	-
Arsenic	-	100	15	-
Barium	5210	-	150	**34,7**
Boron	6390	-	100	**63,9**
Lead	-	1000	100	-
Cadmium	-	15	3	-
Chromium total	93	1000	100	0
Cobalt	707	100	50	**7 / 14**
Copper	327	1000	100	3,2
Manganese	376	2000		0
Molybdenum	-	20	10	-
Nickel	700	200	50	**3,5 / 14**
Mercury	-	10	1	-
Silver	-	-	2	-
Thallium	-	-	1	-
Vanadium	17	-	25	0
Iron	4500	-	-	-
Zinc	1350	3000	300	0 / 4,5
Tin	-	-	5	-

In the case of total metal content **Co** and **Ni** exceed the relevant sludge limits. Ten times of the relevant soil limits are exceeded by **Ba**, **B**, **Co** and **Ni**.

I will not go into details regarding the toxicological and mutagenetical investigations, the results of these were negative in every case. So from this point of view the waste is non hazardous. Daphnia and alga tests show slight ecotoxical effect.

According to the test results the investigated waste enamel slip could be classed into the III. hazard class because of the results of toxic-metal investigations, if we disregard the classification of the aluminium as toxic metal.

However the value committee classified it as II. hazard class category because aluminium ions can contribute to development of Alzheimer-disease.

During the valuation there was professional debate about the high value of aluminium, as a resulting we got possibility to investigate fresh waste enamel slip for aluminium. Probably this aluminium is not coming from our technology, but this was added to the waste enamel slip as a result of unsuitable storage. This was the official point of view. It did not satisfy us so we carried out further investigations.

Second study

During the classification has arisen that such a high value of aluminium-content of the sample is not typical of the present waste. Though the waste contains fine-grained clay as suspending agent, but considering the low application rate of clay, the high presence isn't clear. To make doubts clear the determination of the aluminium content was made from waste enamel originated in the last few years, collected in container, and disposed at closed place.

The examinations shows, that the aluminium content in distilled-water extract doesn't exceed the ten times value of drinking-water limit. In acetate-buffer extract 126-140 times value of drinking-water limit can be seen, which means that it exceeds the hazard limit and involves III. hazard class classification.

In the case of 2M nitric-acid extract the aluminium content of the second sample decreased (3297 mg/kg) compared to the average aluminium content of the first sample (5113 mg/kg) (**Table 6.**).

Table 6.

	Aluminium-content (mg/kg) in the extract		
	Distilled-water	**Acetate-buffer**	**2M Nitric-acid**
W1	61,7	2,3	5113
W2	0,83	14	3297

Compared to this decrease the dissolving in water was smaller. This shows, that aluminium is found in other chemical bond in fresh waste. The higher dissolving in acetate-buffer seems to prove this.

The aluminium was found in the second sample too, but the soluble part in water is under the limits and the value typical of III. hazard class appear only in the acetate-buffer extract. As a result of these investigations our present waste enamel slip was classified as III. hazard class.

Third study

Although we managed to class the waste into lower class with the later investigation, the statements up till now didn't satisfy me, since it is contradictory for me, that the aluminium bonded in a clay mineral should have any effect on the environment, in spite of the fact, that waste enamel in present state was classed hazardous by the final results of the investigation because of other components.

Since the second sample was objected to further investigation. There was supposed not only dissolved Al-ions but also Al from fine clay particles are measured causing false result.

There were preparing two samples during the filtering. One of them was subjected to centrifuging at a rotation frequency of 4500 min^{-1} for 10 minutes before filtering.

The amount of aluminium in the sample treated by centrifuging was approximately a tenth part compared to the untreated sample (**Table 7.**)

Table 7.

	Amount of the aluminium (mg/l)	
	Treated by centrifuging	**Untreated**
W1		44
W2	0,83	
W3	0,6	7

Test results show, that aluminium content of the sample decreases in consequence of centrifuging. It seems to be likely, that in the case of the first sample the more hundred times limit exceeding may not caused by the aluminium ions, but it comes from the measuring of the aluminium bonded in clay-grains with covalence in crystal. Solid particles with size less than 1 mm introduced into the Ar plasma during nebulization of sample solution were dissociated into atoms at a temperature of 6000-7000 K. Consequently without centrifuging the amount of the aluminium bonded in suspended solid particles and the aluminium dissolved as ions, while with centrifuging only the amount of aluminium dissolved as ions are determined by ICP-AES technique.

The enamel frit particles less than 1 mm can also break through the filter and make the test results false. It would be professionally wrong to classify non hazardous waste as hazardous because of such a fault. To prove this supposition and adjust the standard will be one of the future tasks.

Fourth study

We would like to know if it is possible to transform the waste enamel, which has got "III. hazard class" classification by now, into waste with "non hazard class" classification. It was most obvious for us to smelt through the waste enamel slip after drying and homogenising. With this procedure we obtain an enamel frit with unknown composition, which has a smaller surface, than the surface after grinding. During the examination the first study was repeated with the transformed waste enamel. During preparation of extract the centrifuging before filtering was also made.

Test results

Results of the investigations of physical and chemical properties

Table 8. shows results of the resmelted sample investigations in comparison with the untreated waste results.

Table 8.

Investigated parameter	Unit	Resmelted waste	Untreated waste	Limit exceeding x (times)
Dry solids content	%	**99,84**	78	-
Ignition loss	%	**0,08**	2,3	-
Easily dischargeable cyanides	mg/kg	-	0,02	**0**
Total cyanides	mg/kg	-	0,08	**0**

There are no reprehensible parameters among the results of resmelted sample investigations.

Table 9. shows results of investigations of distilled-water extract. There are no components values to exceed hazardous limit (ten times of the value of drinking-water limit) in distilled-water extract. The pH value meets the requirements.

Table 9.

Investigated parameter	Unit	Resmelted waste	Untreated waste	Limit exceeding x (times)
pH		**7,63**	9,5	
El.conductivity	mS/cm	**61**	523	**0**
COD	mg/l	**17**	29,3	**1,1**
Nitrite	mg/l	**0,22**	0,50	**2,2**
Nitrate	mg/l	**1,9**	1,1	**0**
Fluoride	mg/l	**0,4**	11,6	**0**
Chloride	mg/l	**7**	43	**0**
Sulphate	mg/l	-	22	-
Sulphide	mg/l	-	0,5	-
Ammonia	mg/l	-	0,57	-
Anionactive det.	mg/l	**0,05**	0,01	**0**

Investigation of the influence of the quantity and of the environmental effects of mobile

components

Table 10. shows results of toxic-metal investigations in comparison with the untreated waste results in distilled-water and acetate-buffer extracts.

Table 10.

Investigated element	Resmelted waste Distilled water extract (mg/l)	Untreated waste Distilled water extract (mg/l)	Resmelted waste Acetate-buffer extract (mg/l)	Untreated waste Acetate-buffer extract (mg/l)	Limit exceeding x (times)
Aluminium	**0,05**	43	**0,22**	2,3	**0**
Arsenic	**-**	-	**-**	-	**-**
Barium	**0,123**	1,5	**0,625**	9,7	**0**
Boron	**0,3**	33	**2,37**	43,3	**0**
Lead	**-**	-	**-**	-	**-**
Cadmium	**-**	-	**-**	-	**-**
Chromium total	**-**	2,1	**-**	0,45	**0**
Chromium VI	**-**	1,1	**-**	-	**-**
Cobalt	**0,009**	1,4	**0,175**	-	**-**
Copper	**0,009**	0,2	**0,030**	0,11	**0**
Manganese	**0,005**	0,2	**0,035**	0,1	**0**
Molybdenum	**-**	-	**-**	-	**-**
Nickel	**0,012**	0,7	**0,47**	-	**0**
Mercury	**-**	-	**-**	-	**-**
Silver	**-**	-	**-**	-	**-**
Thallium	**-**	-	**-**	-	**-**
Vanadium	**0,005**	0,26	**0,005**	0,1	**0**
Iron	**0,04**	8,6	**0,165**	0,8	**0**
Zinc	**0,045**	4,3	**1,11**	0,63	**0**
Tin	**-**	-	**-**	-	**-**

In the case of mobile metals there are no values exceeded the hazardous limit, namely in distilled-water extract more than ten times, in acetate-buffer extract more that hundred times exceeding of the drinking-water limit.

Table 11. shows results of the toxic-metal investigations in comparison with the untreated waste results in 2M nitric-acid extract.

In the case of total metal content there are no exceeding regarding to ten times of the sludge and soil limits.

Summarising we can state, that in the case of the above examinations the waste enamel frit treated by smelting meets the criteria of "non hazard waste" according to the results of physical and chemical investigations. Of course, performed investigations are only informative.

Table 11.

Investigated element	Resmelted waste Metalcontent (mg/kg)	Untreated waste Metalcontent (mg/kg)	Limit exceeding x(times)
Aluminium	**15,9**	7420	**-**
Arsenic	**-**	-	**-**
Barium	**14,6**	5210	**0**
Boron	**6,6**	6390	**0**
Lead	**-**	-	**-**
Cadmium	**-**	-	**-**
Chromium total	**-**	93	**-**
Cobalt	**9,4**	707	**0**
Copper	**0,9**	327	**0**
Manganese	**0,64**	376	**0**
Molybdenum	**-**	-	**-**
Nickel	**12,4**	700	**0**

Mercury	**-**	-	**-**
Silver	**-**	-	**-**
Thallium	**-**	-	**-**
Vanadium	**0,4**	17	**0**
Iron	**40,7**	4500	**0**
Zinc	**10,5**	1350	**0**
Tin	**-**	-	**-**

Test results shows, that in the case of waste treated by smelting nearly all values are smaller in order of magnitude, than in the case of the untreated waste. Hazardous components are bonded strongly to the glass-matrix due to the transformation, the contact surface decreases significantly, and leaching can't be taking into account (pH value).

Summary

The examinations show that:

- storage of the waste can influence the results of the classification
- while taking samples for classification one has to take care that only material in ion state get into the solution. The standard should be changed by precisely describing the way of filtering and centrifuging during the preparation of the sample, specially regarding those wastes, where because of their composition and physical state, one can count with microparticles getting into the examined solution.
- to develop one waste-transforming technology needs consideration to gain "non hazardous waste" classification

Note: *The classification of waste enamel slip of Lampart Rt. does not automatically mean that waste enamel slip of other companies can be classified in the same category. Each waste has to be classified individually.*