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IMPLEMENTATION OF THE CONFORMATION MEASURES OF THE ECONOMICAL AGENTS TO THE NATIONAL LEGISLATIVE REQUIREMENTS REGARDING THE LIMITATIONS OF VOLATILE ORGANIC COMPOUNDS EMISSIONS

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Abstract. On the European level the concernments regarding the limitation of volatile organic solvents have been put across by the 1999/13/EC Directive (VOC Directive) approval. In Romania, according to the liabilities assumed by the 22nd Chapter – Environmental Protection, in the 'Measures for intensification and acceleration of preparations regarding the EU adherence program', the mentioned directive was fully transposed by enactment of Government Decision (GD) 699/2003 (modified by GD 1902/2004) and Minister Order (MO) 859/2005. The goal of this act is to prevent or to reduce the direct or indirect effects of volatile organic compound emissions in the environment, mainly in air. There are presented the results obtained in the framework of the studies regarding the legislative implementation which regulates the reduction measures of the VOC emissions, in the activities of footwear fabrication and overlay, lacquer, ink and adhesives fabrication.

Keywords: VOC, emissions, solvents, management plan.

AIMS AND BACKGROUND

Within industrial activities from different sectors are used very large quantities of chemical organic substances, which by volatilisation are producing negative effects to the environment constituents, especially to the air.

Those substances are known as volatile organic compounds (VOC), being introduced in the industrial processes in pure state or in mixture with other compounds which they are dissolving. The main classes of substances from which result the VOC frequently used in industrial activities as staples, are: aliphatic hydrocarbons, aromatic mononuclear hydrocarbons, halogen compounds of alkanes, alkenes, alcohols, ketones, esters and organic derivates with nitrogen.

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All those compounds are used to dissolve staples in order to obtain finite products, as cleaning agents to dissolve the impurities, as spreading environment, sliminess regulator, superficial tension regulator, plasticisers or preservers.

Because of the high volatilisation, a great part of these compounds, through all the technological phases (transportation, dosing, mixing, filtration, packing, storage) are released into the air as gaseous emissions, having a negative impact for the quality of this environmental constituent. In time, once with the climatic conditions modification (temperature decrease, precipitation appearance), a part of the volatile organic compounds, through condensation, or entrapment by the precipitation water is returning on soil, damaging its quality and affecting, in a negative way, the vegetation growing. It's not less important the negative effect produced by VOC to the surface waters or internal waters, even if their solubility in water is, in most of the cases, very low.

The strongest negative effects, produced by VOC emissions, are recorded in the environmental constituent – air, consisting in the ozone layer modification, with direct impurities in the decreasing of the photosynthesis process and most of all affecting human health. The existence of big concentrations of VOC in the air, in working environments and in the neighbourhood locations caused an immediate effect for the service personnel or for the population in the area, the dizziness, headaches, eyes and respiration irritation appearance.

On long terms, take place the memory weakening, the appearance of some allergic reactions and, in some cases, the appearance of different cases of cancer.

Because of these reasons, the most part of VOC are classified as dangerous chemical substances, and to some of them have been attributed the risk phases R.45, R.46, R.49, R.60, R.61 and R.40, being registered as cancerous, mutation or toxic substances, for reproduction (CMR solvents).

Taking into account all these aspects, in the last years, on the world and national plan preoccupations regarding the decrease of VOC emissions level are demonstrated. These preoccupations have been settled on world level by emitting and approving protocols and conventions[1–5].

On the European level have been emitted and approved 1999/13/EC Directive[6], transposed in the Romanian environment legislation by GD 699/2003 modified and completed by GD 1902/2004 (Ref. 7). In correlation with this settlement has been emitted the Minister Order of Environment and Water Administration– MO 859/2005 (Ref. 8). The scope of these normative documents is to identify and apply measures and procedures for reduction of VOC emissions in order to correspond the economical agents to the legislative requirements and to reduce the negative effects of the polluting elements caused by certain activities.

Methods. For the implementation of the accordance measures imposed by GD 699/2003, modified and completed, had been made case studies to the economical agents, with activities of footwear fabrication and overlay, lacquer, ink and adhesives fabrication.

The work methodology, generally valid for all the activities included in Table No1 from Annex No2 to GD 699/2003, modified and completed, is consisting in doing the Management Plan of organic solvents with VOC content. This has in its structure the following three components:

– solvents balance;

– VOC emissions reducing scheme (plan);

– VOC emissions monitoring scheme.

For the solvents balance are established the solvents consumption (SC) for the activity analysed in order to verify if threshold value is overpassed and is proved the conformity or unconformity to the limit values for the fugitive emissions, total emissions or goal value of the reducing plan.

The reducing scheme includes methods which the titular of the activity must apply in a determined period of time, so that he can obtain VOC emissions reduction until it is harmonising with the limit values.

VOC emissions monitoring scheme allows VOC quantification in the solvents balance processing and assures the function capacity self-control of the emissions purifying/ reduction installations.

The following notions are used in realising the solvents balance:

- SC – solvents consumption;
- I – organic solvents inputs from the activity;
- O – organic solvents outputs from the activity;
- E – total emission;
- F – fugitive emission.

OBS. Solvents balance is realised for a one-year period of time. All used notions refer to this period of time.

Inputs:

➢ I – the quantity of organic solvents that contain volatile organic solvents used in the input of the technological process; the input of the organic solvents in the technological process can be done by two fluxes (I1 and I2);

➢ I1 – the quantity of organic solvents or their quantity in preparation purchased which are used as input into the process in the time frame over which the mass balance is being calculated;

➢ I2 – the quantity of organic solvents or their quantity in preparations recovered and reused as solvent input into the process, for the year over which the mass balance is being calculated.

Outputs: Quantities that result from the installation in one year

- O1 – the quantity of volatile organic solvents emissions in waste gases (captivated emissions or controlled emissions);
- O2 – the quantity of organic solvents lost in waste water;
- O3 – the quantity of organic solvents which remains as contamination or residue in products output from the process;
- O4 – the quantity of volatile organic solvents to air, from emissions that were not captivated (uncontrolled); coming from the general ventilation of rooms, where air is released to the outside environment via windows, doors, vents, and similar openings;
- O5 – the quantity of organic solvents and/or organic compounds or physical reactions (including for example those which are destroyed, by incineration or other waste gas or waste water treatments, or captured, by adsorption, as long as they are not counted under O6, O7 or O8);
- O6 – the quantity of organic solvents contained in collected waste;
- O7 – the quantity of organic solvents or organic solvents contained in preparations, which are sold or are intended to be sold as a commercially valuable product;
- O8 – the quantity of organic solvents contained in preparations recovered for reuse, but not as input into the process, as long as not counted under O7;
- O9 – the quantity of organic solvents released in other ways.

Calculation formulas of the solvents balance are:

- SC= I1 – O8 (kg/year);
- E = F + O1;
- O1= I1 – O5 – O6 – O7 – O8

F can be determined by one of the following methods:

- *Direct method*: F = O2 + O3 + O4 + O9
- *Indirect method*: F = I1 – O1 – O5 – O6 – O7 – O8.

RESULTS

CASE STUDY (1). ORGANIC SOLVENTS MANAGEMENT PLAN FOR THE ACTIVITY OF FOOTWEAR FABRICATION

In the activity of footwear fabrication are known in the present three techniques, as follows:

- Footwear fabrication technique ‘by manufacturing’;
- Footwear fabrication technique ‘by injection’;
- Paste method with fused mass on hit.

From all these techniques, only the first one is generating meaningful VOC emissions. In this technique, polymethanic and/or polychloroprenic adhesives are being used, based on organic solvents containing VOC. The classes of existing VOC

in the materials used in footwear fabrication 'by manufacturing' are: hydrocarbons, halogen compounds, alcohols, ethers, carbonyl compounds, esters, amides.

VOC emissions are generated in the following points of the technological flux:

– applying polychloroprenic adhesive;
– grease outside with adhesive;
– grease sole with adhesive;
– grease and applying insole roof;
– finishing.

The necessary measures for the accordance with legislative requests from HG 699/2003 modified and completed, for this activity are:

– threshold value: under 5 t organic VOC/year;
– total emission value (E): under the limit of 25 g VOC/year.

For the realisation of the case study, the activity of an economical agent from Bucharest, fabricating footwear by the 'by manufacturing' technique, was analysed. Organic solvents containing VOC Management Plan was realised for the 01.01.2005-31.12.2005 period. The data referring to the quantities and composition of adhesives and products based on organic solvents, used in this period of time are compressed in Table 1.

Table 1. Inputs (I1) of material with organic solvents containing VOC 01.01.2005–31.12.2005 period

No crt.	Name of the material containing organic solvents with VOC	Organic solvents with VOC (%) content	The quantity of material used in the referenced period (kg)	The quantity of organic solvents with VOC used in the referenced period (kg)
0	1	2	3	4
1	POLIGRIP R 385	85	864	734.4
2	POLIGRIP M 315	62.5	800	500
3	POLIGRIP M 329	84.4	5888	4969
4	POLIGRIP M 1	62	853	528.9
5	ULTRAPUR S-21	60	255	153
6	ULTRAPRIMER 401	60	135	81
7	DESMODUR	75	134	100.5
8	APN 4104	27	5232	1412.6
9	AX 1820	25	600	150
10	HALOGENO-MONO	97	215	208.6
11	CLEANER 47 S	100	1372	1372
12	CLEANER G 425	100	50	50
13	CLEANER 509	90	50	45
	Total			10305

The data from columns 1 and 3 are taken from the staple consumption evidence from the economical agent and the ones from column 2 are taken from the technical files of the products.

The data from column 4 were obtained with the formula:

$$\text{col. } 4 = \text{col. } 2 \times \text{col. } 3 /100$$

From the presented data in Table 1 results that:

$$I1 = 10305 \text{ kg} = 10.305 \text{ t/year.}$$

In the economical agent activity are not recovered organic solvents containing VOC. So:

$$O8 = 0 \text{ t/year.}$$

With these data, the consumption of solvents for the referenced period is:

$$SC = I1 - O8 = 10.305 \text{ t / year.}$$

It is noticed that threshold value is overpassed (5 t/year) and the determination of total emissions (E) is necessary.

For this activity, total emissions are expressed as specific consumption, by comparing the quantity of VOC emissions in the environment to the total number of footwear pairs obtained in the referenced period.

Because in the analysed activity there are no lost of VOC through chemical and physical processes (O5=0), are not calculated wastes that contain VOC (O6=0), VOC is not found in the final product (O7=0) and VOC is not recovered (O8=0), it results that practically all VOC quantity entered into the process is emitted into the atmosphere. As a consequence:

$$E = I1 = 10.305 \text{ t/year.}$$

In the 1-year reference period, the economical agent obtained 133.205 pairs of footwear. With data, we can obtain:

$$E = 10.305 \times 10^6 /133.205 = 77.36 \text{ g VOC/pair.}$$

The limit value being 25 g VOC/pair, results that the developed activity is in conformity with the settlements of GD 699/2003, modified and completed. In this case, the elaboration of VOC emissions Reducing Scheme (Plan) is imposed.

The establishment of the optimum VOC emissions reduction method, contained into the Plan, takes into account the following criterions:

- Reducing level of the emissions by applying the technological solution studied, related to the overpass of their limit values;
- The necessary investment to buy the installation appropriate to the chosen technological solution;
- Liquidation period for investment;
- Implications on the cost value for the final product;

➢ Adaptability level of solution (installation) at the fabrication networks change in order to diversify the products.

Based on the 'Best Available Techniques' procedures for the activity of footwear fabrication and a criterions mentioned before, VOC emissions reduction Plan, for the economical agent for whom the case study have been elaborated, includes the following measures:

➢ Partial or total replacement of the adhesives based on organic solvents with free of these compounds adhesives;

➢ Using some paste techniques with adhesives free of solvents;

➢ Using an residual gases purifying installation by adsorption, bio-filtration or after-combustion;

➢ Reducing the specific consumption of adhesives based on organic solvents – for a better administration.

Monitoring Scheme will be elaborated based on the principles mentioned below:

➢ A rigorous monitoring is done for the specific consumption of materials that have in their composition organic solvents with contents of volatile organic solvents in order to determinate their total emissions;

➢ In the administration register of the amounts of material that have in their constitution volatile organic compounds, to specify in the storehouse card or in other administration document, the exact composition of the products, either by asking it to the producer, or by sampling some samples and analysing them in specialised laboratories;

➢ It is recommended that, even if the legislative requests are not referring to the exact value of the emissions in the residual gases, directional or fugitive, periodically the economic agent must analyse the content in volatile organic compounds of the emissions, in order to find the best methods to reduce them.

CASE STUDY (2). ORGANIC SOLVENTS MANAGEMENT PLAN FOR THE ACTIVITY OF OVERLAY, LACQUER, INK AND ADHESIVES FABRICATION

Main phases of the technological process and the sources of VOC emissions:

A. Preparation of the past – VOC emissions in the air;
B. Mixing (homogenising) – VOC emissions in the air;
C. Impastation (rubbing the paste) – VOC emissions in the air;
D. Finishing the product – VOC emissions in the air;
E. Packing the product – VOC emissions in the air;
F. Washing the equipment – VOC emissions in the air;
   – VOC emissions in the waste.

The necessary measures for the accordance with the legislative requirements in this activity are grouped in two intervals:

Threshold values:

(a) 100-1000 t/year organic solvents: C <150 mg C/N m^3; F<5%; E<5%.

(b) >1000 t/year organic solvents: C <100 mg C/N m^3; F<3%; E<3%.

The case study was elaborated based on the data offered by the economical agent from Bucharest for a 1-year reference period, 01.01.2005–31.12.2005 period.

The organic solvents containing VOC used in the technological process are entering in this process by two ways:

– as pure solvents;

– as resins.

The data referring to the two types of entries are presented in Tables 2 and 3.

Table 2. Necessary data in order to establish the volatile organic compounds inputs from the organic solvents in 2004

No	Organic solvent name	Chemical formula	Stock (kg) 01.01.04	Inputs (kg) 2004	Stock (kg) 31.12.04	Consumption (kg)
1.	Butyl acetate	$C_6H_{12}O_2$	1057.50	37012.00	558.50	37511.00
2.	Ethyl acetate	$C_4H_8O_2$	96.20	11140.00	50.60	11185.60
3.	Isobutyl acetate	$C_6H_{12}O_2$	0.00	6834.00	326.50	6507.50
4.	Acetone	C_3H_6O	1068.90	23357.00	818.85	23607.05
5.	Tehnical ethanol	C_2H_6O	694.73	897.00	5.80	1585.93
6.	Ethanol denatured	C_2H_6O	0.00	1468.00	520.50	947.50
7.	Arcosolv PM	$C_4H_{10}O_2$	1284.27	41207.00	0.00	42491.27
8.	Extraction petrol		417.00	2670.00	1210.00	1877.00
9.	Butyl di-glycol	$C_8H_{18}O_3$	199.07	200.00	224.80	174.27
10.	Butyl glycol	$C_6H_{14}O_2$	112.50	190.00	253.00	49.50
11.	Cyclohexane	C_6H_{12}	75.00	304.00	145.00	234.00
12.	Diluent S010	C_8H_8	301.40	11075.00	185.00	11191.40
13.	Diluent T050	C_7H_8	0.00	5523.00	0.00	5523.00
14.	Diluent X060	C_8H_{10}	0.00	537.00	0.00	537.00
15.	Dowanol DPNB	$C_{10}H_{22}O_3$	158.32	7030.00	302.00	6886.32
16.	Ethyl glycol	$C_4H_{10}O_2$	88.00	360.00	180.00	268.00
17.	Ethyl methyl ketone	C_6H_8O	9.56	8346.00	16.30	8339.26
18.	Methoxy-propyl-acetate	$C_6H_{12}O_3$	80.40	4280.00	245.00	4115.40
19.	1-Butanol	C_4H_9O	1312.82	21739.00	45.94	23005.88
20.	Propyl glycol	$C_3H_8O_2$	39.20	11871.00	1655.60	10254.60
21.	Distilated solvent	70% toluene + 10% acetone + 20% xylene+ white spirit	0.00	5284.00	0.00	5284.00
22	TBA 95 Solvent	95% toluene + 5% butyl acetate	0.00	4400.00	0.00	4400.00
23	Styrene	C_8H_8	0.00	3840.00	75.00	3765.00
24	Toluene	C_7H_8	20511.00	358020.00	23560.00	354971.00
25	White spirit	$C_{12} – C_{18}$ or C_nH_{2n+2} with n = 12 – 18	7725.81	72120.00	3994.00	75851.81
26	Xylene	C_8H_{10}	9733.00	78140.00	0.00	87873.00
	Total		44964.68	717844.00	34372.39	728436.29

Table 3. Necessary data in order to establish the volatile organic compounds inputs from the resins in 2004

No	Resin name	Organic solvent content (%)	Stock (kg)	Inputs (kg)	Stock (kg)	Resins consumption (kg)	VOC consumption (kg)
			31.12.03	2004	31.12.04	2004	2004
1	AZAMIN M514	60% isobutanol	1715.10	7110.00	995.00	7830.10	4698.06
2	AZAMIN U301	60% isobutanol	472.50	2000.00	512.00	1960.50	1176.30
3	BAYSILONE M120	50% xylene,butanol	246.00	2800.00	225.00	2821.00	1410.50
4	BECKOPOX EH 651	70% xylene	0.00	25200.00	0.00	25200.00	17640.00
5	DER 671	75% xylene	642.33	80300.00	1100.00	79842.33	59881.75
6	EPIKURE 3115/70	70% xylene	0.00	180.00	0.00	180.00	126.00
7	ESAPOL 45	66% styrene	649.00	56096.00	665.00	56080.00	37012.80
8	ESTAL 19 – 55%	55% xylene, butanol	3031.50	132772.00	987.00	134816.50	74149.07
9	ESTAL 19 – 60% X	60% xylene	0.00	1400.00	0.00	1400.00	840.00
10	ESTAL 19 – 55%TB	55% toluene, butanol	0.00	2000.00	0.00	2000.00	1100.00
11	ESTAL 19 A	55% xylene, butanol	724.16	3600.00	0.00	4324.16	2378.29
12	ESTAL 32	65% white spirit	1710.55	84152.00	2637.00	83225.55	54096.00
13	ESTAL 32O	65% white spirit, xylene	0.00	3805.00	705.00	3100.00	2015.00
14	ESTAL AC 1	65% xylene,toluene	31.80	15525.00	800.00	14756.80	9591.92
15	ESTAL D50T	50% toluene	464.00	11000.00	804.00	10660.00	5330.00
16	ESTAL RD 1	60% xylene	0.00	11000.00	242.00	10758.00	6454.80
17	MELAROM 514	60% isobutanol	0.00	5600.00	122.00	5478.00	3286.80
18	SYNTHALAT A077	65% xylene	6306.60	20590.00	5671.00	21225.60	13796.64
19	SYNTHALAT SF 270	60% xylene	541.00	11200.00	3351.40	8389.60	5033.76
20	TOLONATE HDB 75 MX	75% propylene glycol mono-methyl ether acetate	0.00	4300.00	0.00	4300.00	3225.00
21	UREZIT 35	60% isobutanol	0.00	540.00	253.00	287.00	172.20
22	WORLEEKYD B865U	55% white spirit	1164.00	5100.00	1872.10	4391.90	2415.55
	Total		9686.94	444540.00	9794.00	444432.94	305831.04

The processing of the data from the two tables allows concluding that:

$$I1 = 728436.29 + 305831.04 = 1034267.3 \text{ kg/year}$$

or

$$I1 = 1034.267 \text{ t/year}$$

From analysing the technological process based on the data given by the economical agent, it results the following aspects:

– in 2004 resulted from the equipment wash processes a quantity of 39.533 t mixture of VOC and solid compounds, called 'dirty solvent';

– by its distillation are obtained 27.089 t of solvent recovered and 10.719 t waste as 'slime' that contains 14.5% VOC; total quantity of VOC from waste (O6) is $10.719 \times 14.5/100 = 1.554$ t;

– from the 27.099 t as I2 returned into the process and the rest of 0.99 t was stoked in order to reuse it next year (O8);

– in the technological process there is no lost of organic solvents after chemical reactions (O5=0);

– the quantity of organic solvents containing VOC, for commercialisation as they are or in the composition of the eradicators (O7) was determined from the society book-keeping and has the value of 954.922 t.

With data, is obtained:

$$SC = 1034.267 – 0.99 = 1033.277 \text{ t/year}$$

$$SC > 1000 \text{ t/year.}$$

The activity is framed in the second threshold level

$$E = 1034.267 – 1.554 – 954.922 – 0.99 = 76.801 \text{ t/year}$$

$$I1+I2 = 1034.267+26.099 = 1060.266 \text{ t/year.}$$

By comparing total emissions (E) to the total inputs (I1+I2) in a period of one year, we obtain:

$$E= 76.809 \times 100/1060.366 = 7.2 \%.$$

The limit value imposed for E for SC > 1000 t/year is: E>3%.

In conclusion, the developed activity is in conformity with the settlements of GD 699/2003, modified and completed. Is mandatory the elaboration of the reducing Scheme (Plan).

The reducing Plan, elaborated based on BAT procedures, includes the following measures:

(a) general measures: personnel instruction, optimising fabrication and control process, introducing the environment management system;

(b) measures for reducing the emissions in the air: closing and sealing the components of the installation, assembling equipments of purification and retain of the VOC from the residual gases;

(c) measures for reducing the emissions in the water: collecting and treating the residual waters, monitoring the lost of VOC in the residual waters;

(d) measures regarding solid wastes: reducing the quantities, recovering, recycling, destroying, putting good use in other activities;

(e) measures regarding the administration of the dangerous chemical substances: replacing some staples, respecting the stipulations referring to CMR substances and their replacement.

Monitoring Scheme has in its structure:

- establishing the emission points: special attention in the determination of the VOC emissions in the residual gases;
- establishing the sampling frequency;
- intensification of the monitoring activity of the point-like and diffuse evacuation sources in which there are noticed frequent surpasses of the limit values;
- determination of the volumetric capacity of the residual gases;
- recording in the charge files the times for each operation;
- capacity countering determination of the residual water and determination of VOC from it.

CONCLUSIONS

From the elaborated case studies, is resulted a series of difficulties in the implementation of the conformation measures of the economical agents to the national legislative requirements regarding the VOC emissions limitation.

These difficulties are referring to:

– exaggerated restrictive value for considering one organic compound as being volatile (vapour pressure > 0.01 kPa for 293.15 K);

– confuse definitions: cataloging the emissions of residual gases directional ore untreated, as being diffuse emissions;

– contradictory limit values: for some activities, C<150 mgC/Nm^3 in case of installations provided with equipments for gases treatment and C<20 mgC/ Nm^3 for those without equipments for gases treatment;

– the impossibility of quantification for some kind of outputs: O4 and O9;

– difficulties in the correct quantification of the O1 outputs;

– discontinuity of the processes and the great variety of products obtained from some activities, involving a great number of VOC, are making impossible an exact solvents balance.

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