Elimination of Odors Emitted from Hot-Melting of Recycle PS by Oxidative-Reductive Scrubbing

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ABSTRACT

Hot-melt granulation of waste plastics emits fumes with unpleasant plastic-burning odor during the heating process. This study uses sodium hypochlorite (NaOCl) solution to scrub and oxidize the volatile organic compounds (VOCs) and the associated odors from polystyrene (PS) hot-melting exhaust. An alkaline hydrogen peroxide (H_2O_2) solution was followed to remove Cl_2 emitted from the oxidative solution. Laboratory scrubbing bottles with a liquid volume of 600 mL were used with the hot melt gas injected into the system at a rate of 1 L/min at 25°C.

Results indicate that by purging the test gas through a solution with an available chlorine of 300–370 mg/L at an adjusted pH (6.5–7.0) for oxidation of the absorbed odorous compounds, and then through a solution with pH > 12.0 and 0.35% H_2O_2 for absorption and reduction of Cl_2 (< 11.2 ppm) in the exhaust gas from the oxidation liquid, around 90% of the VOCs in the range of 3.2–55.5 ppm (expressed as methane equivalent) was removed.

Estimations indicate that it requires around 1.62, 0.0452, and 0.0827 kg NaOCl solution (12% available Cl_2), H_2O_2 solution (35% H_2O_2), and sodium hydroxide solution (45% NaOH), respectively, for scrubbing 1,000 m^3 of the exhaust gas with 10 ppm NMHC (expressed as methane equivalent). The chemicals cost a total of approximately USD 0.32.

The study has developed a new, effective and economic process for reducing odorous compounds in the hot-melted gas. When commercialized the process is hoped to decrease a lot of odorous complaints.

Keywords: Renewable polystyrene; Hot melt; Sodium hypochlorite; Hydrogen peroxide; Odor control.

INTRODUCTION

Sources of odor generated in plastic recycling processes mainly come from fumes produced by the hot (150 to 250°C) extrusion granulation process. Field experiences indicate that nylon recycling produces the smells of ammonia and burnt plastics and polypropylene (PP) plastic recycling produces mainly the smell of acrolein from oxidation of propylene on pyrolysis of PP. Based on a study by Tsai *et al.* (2009), melting of polyethylene (PE)/PP/polyvinyl chloride (PVC) waste plastics produces odor downwind of a plant's perimeter at concentrations of 100 to 229 (dimensionless, dilution times to odor threshold), which is higher than the regulation upper limit of 50 for industrial area set by the Environmental Protection Administration of Taiwan.

Related studies have been done by some researchers. Yamashita *et al.* (2009) showed that hot-melt virgin PS emits aromatic hydrocarbons and aldehydes as main organic compounds as shown in Table 1. All the emitted volatile organic compounds (VOCs) shown in Table 1 are harmful to the plant's workers and the neighboring inhabitants and the associated odor may raise public complaints. Other studies have also reported various VOC emission factors or compounds (Hoff and Jacobsson, 1981; Forrest *et al.*, 1995; Barlow *et al.*, 1996; Adams *et al.*, 1999; Xiang *et al.*, 2002).

As indicated in Fig. 1, for control of the emitted fumes to prevent them from venting to the operation area and the plant's perimeters, emitted fumes should be collected by two hoods, one set at above the gas vent hole located at approximately the middle point of the heated screw smelter and the other at the exit end of the smelter. The collected gas streams are then combined and conducted to a control system. In general, an electrostatic precipitator (ESP) is used to remove the mists in the collected gas and the mist removal efficiency depends strongly on the size and electrostatic conductivity of the mists. The odorous VOCs should further be controlled to eliminate possible public complaints when contact with the vent gas.

Chemical scrubbing can be used for the control of waste gases with VOCs. Aqueous sodium hypochlorite was found to be among the most effective oxidants. A few studies focused on the hypochlorite oxidation of aqueous organics such as benzene, toluene, xylenes, phenolates, aldehydes, and ketones.
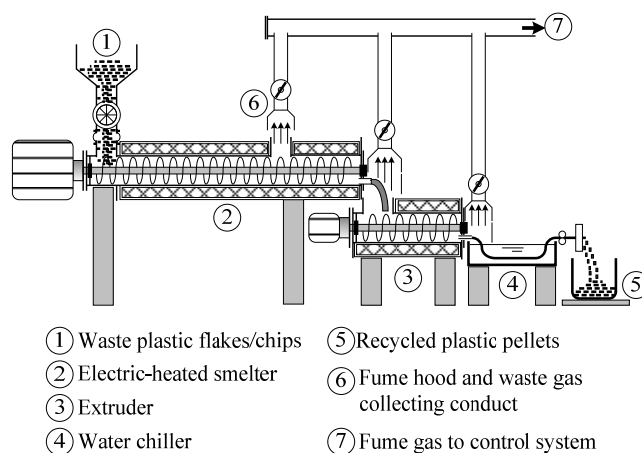
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Table 1. VOC emission factor of plastics heated to 200°C in air (Yamashita *et al.*, 2009).

	Average value of VOC emission factor (mg as toluene/kg plastic)			
	Virgin PP	Virgin PS	Virgin LDPE	Recycled PP/PE/PS
Aliphatic hydrocarbons	320	2	32	220
Aromatic hydrocarbons	0	200	1	10
Alcohols	0	10	2	20
Aldehydes	0	20	18	240
Ketones	0	15	13	80
Esters	0	2	2	70
Organic acids	15	9	9	170
Others	0	2	39	140
Total	335	260	116	950

① Waste plastic flakes/chips   ⑤ Recycled plastic pellets
② Electric-heated smelter   ⑥ Fume hood and waste gas
③ Extruder   collecting conduct
④ Water chiller   ⑦ Fume gas to control system

Fig. 1. Schematic diagram of a plastic smelting and extrusion system, the length of the main smelter (2) is around 4–5 meters.

Chungsiriporn *et al.* (2006) proposed the removal of toluene from waste air using a spray wet scrubber combining the absorption and oxidation reaction. Aqueous sodium hypochlorite (NaOCl) solution was used as the scrubbing liquid in the system. Mirafzal and Lozeva (1998) presented phase transfer catalyzed oxidation of alcohols with sodium hypochlorite in ethyl acetate media that resulted in good to excellent yield of aldehydes or ketones as oxidized products.

Cheng and Hsieh (2010) integrated chemical scrubber with sodium hypochlorite and surfactant to remove hydrocarbons in cooking oil fume. Results indicated that suitable operating parameters of NaOCl scrubber system at pH 6.5, 200 ppm of available chlorine and 11 L/m^3 of liquid/gas ratio were proposed. With the conditions, NMHC (non-methane hydrocarbons) in the cooking fume could be removed from 19 ± 13 to 4 ± 2 mg/m^3 (as methane). The study didn't indicate, however, which components in the fume gas were removed or oxidized.

Chang *et al.* (2011) used sodium hypochlorite (NaOCl) solution in series with alkaline hydrogen peroxide (H$_2$O$_2$) solution in a two-stage scrubbing process to treat the associated odors and VOCs from PP hot-melting operations. VOCs in the hot melt exhaust consist mainly of acrolein, acetone, 2-butanone, and 4-methyl-2-pentanone. Results indicated that by purging the test gas through a solution with an available chlorine of 15–50 mg/L at an adjusted

pH (9.3–10) for absorption and oxidation of the odorous compounds to a degree of around 90%. Following the operation, a solution of 0.35% H$_2$O$_2$ with pH in the rang of 12.0–12.5 was used for absorption and reduction of Cl$_2$ (< 3.8 ppm) in the exhaust gas from the oxidation liquid. Estimations indicated that the chemicals cost a total of approximately USD 0.25 for treating 1,000 m^3 gas.

To the authors' knowledge, there is no report on the removal of VOCs or odorous compounds from waste polystyrene (PS) smelting and extruding processes. In the present study, chemical scrubbing technology using sodium hypochlorite as an oxidant for VOCs and odors and alkaline hydrogen peroxide as a reducing agent for the emitted chlorine from the oxidation liquid was tried to test its applicability to the odor control of the smelting operations for PS recovery. Emission characteristics, effects of pH and concentration of the available chlorine on the VOC and odor removal efficiencies, and if the fixed pH of 12.5 and hydrogen peroxide concentration of 0.35% could remove emitted chlorine in the exhaust gas from the oxidation liquid will be presented in the present study.
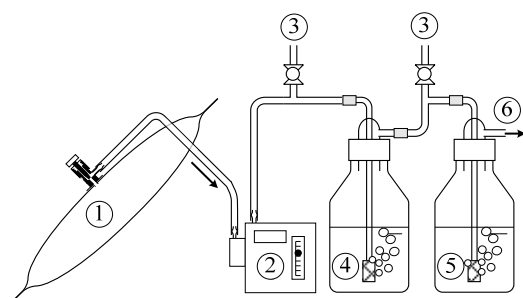
MATERIALS AND METHODS

Experimental

Schematics of the experimental systems are shown in Figs. 2 and 3. Fig. 2 shows a gas generation oven (Hipoint
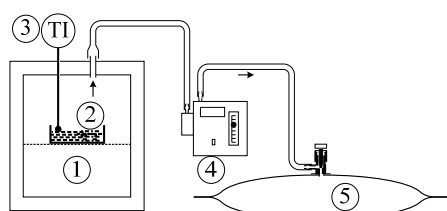
① Oven (40 cm sq. x 40 cmD)   ④ Gas pump (5 L/min)

② Waste plastic chips (800 g)   ⑤ Waste gas storage bag (20L)

③ Temperature indicator

**Fig. 2.** Schematic diagram of the waste gas generation and collection facility.

① Waste gas storage bag (1 L)   ④ Oxidation scrubber (1 L)

② Gas pump (operated at 1.0 L/min)   ⑤ Reduction scrubber (1 L)

③ Gas sampling port   ⑥ Scrubbed gas vent

Fig. 3. Schematic diagram of the chemical scrubbing system.

Precision Oven, Type: OV-40, Taiwan) in which 800 g waste PS plastic chips was placed in an aluminum foil plate and the oven heated to around 160–200°C to melt the plastics. Compared the system shown in Fig. 2 with the field system, the screw extrusion operation shown in Fig. 1 gives the melted plastics a shear force that may crack the polymer chains and emit cracked hydrocarbons. In addition, in an extruder pelletizer, the exposure time of the heated plastics to air is reduced as compared with that in the oven shown in Fig. 2. Hence, setup shown in Fig. 2 could only be partially related to Fig. 1 on the electric heating of the plastic flakes. The emitted gas for test was only a simulated one. Experiences showed that it requires around 30 minutes to heat up the oven to the desired temperature. Fume gas generated after a heating time of 60–90 minutes and it was then drawn by a gas pump (Airchek Sampler, Type: 224-PCXR4, USA) operated at 5 L/min and the collected gas stored in two 20-L Teflon bags for each batch of the melted plastics. A gas sample in each bag was immediately drawn for THC (total hydrocarbon) analysis. Before the absorption test, the gas sample in the 20-L bag was transferred by a sampling pump to a 40-L bag followed by introducing 20 L of the ambient air in the laboratory to the bag. The diluted gas was ready for a scrubbing test.

The scrubbing system shown in Fig. 3 consists of a gas pump and two 1000-mL scrubbing bottles. The first bottle (oxidation scrubber) was filled with 600 mL of aqueous

sodium hypochlorite solution for absorbing and oxidizing the chemicals from the fume gas at a fixed influent flow rate of 1 L/min. The second one (reduction scrubber) contained 600 mL of an aqueous hydrogen peroxide and sodium hydroxide solution for absorbing and reducing the chlorine gas stripped from the oxidation solution. The associated reductive chemical reaction is:

$$Cl_2 + H_2O_2 + 2\ NaOH \rightarrow O_2 + 2\ NaCl + 2\ H_2O \qquad (1)$$
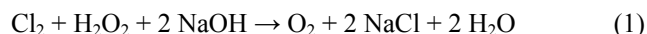
The gas and the scrubbing liquors were all kept at 23–27°C.

In the course of reaction, gas samples were collected by sampling bags for analysis of THC (total hydrocarbons), NMHC (non-methane hydrocarbons), Cl_2, and odor intensity. Scrubbing liquors were also sampled for analysis of pH and residual chlorine. After each test, initial concentration of sodium hypochlorite or pH was adjusted to test its gas cleaning effect. Hydrogen peroxide solution in the second bottle was kept at an initial concentration of 0.35% and adjusted to pH 12.5 by 25 wt% NaOH solution. Around 34 mL of the NaOH solution or 10 g pure NaOH was required for 1 L of the hydrogen peroxide solution.

Materials

Waste PS plastics (mostly containers for instant foods) used in this study were collected from community recycling stations. The collected plastic material was cut into pieces of approximately 1×1 inch in size and water washed. The recycled material contains metal oxide pigments which may catalyze the cracking of polymer chains and oxidation of the cracked hydrocarbons. Actually, some virgin PS pellets are manufactured by blending pigmented and non-pigmented PS pellets before being fed into pellet machines. Therefore, properties of the simulated emitted gas are believed to be similar to those emitted from commercial machines.

All chemicals (aqueous sodium hypochlorite solution with 12 wt% available chlorine, 35 wt% aqueous H_2O_2 solution, and sodium hydroxide) are reagent grades.

Analytical

THC and NMHC concentrations in gas samples were analyzed with a portable flame ionization detector (FID, Thermo, TVA-1000B, USA). Compositions of VOCs in gas samples were analyzed by a gas chromatography (6890N Series GC System, Agilent, USA) and a mass spectrometry (5973 Network Mass Selective Detector, Agilent, USA).

A chlorine analyzer (ToxiRAE II, 045-0516-000, USA) was used for the analysis of gaseous chlorine concentrations. Colorimetry method (USEPA, 1983) was used for the detection of residual chlorine in the scubbering liquor. A pocker colorimeter (Cat No.58700-00, HACH Co., Japan) was used for the color determination.

The "triangle odor bag method" used in Japan since 1972 was used to evaluate the odor intensity of the gas samples (Iwasaki, 2003). The method is an air dilution approach using statistical methods in which "odor index" is measured. The odor intensity or concentration is expressed as dilution times (dimensionless) to threshold.

RESULTS AND DISCUSSION

Effects of Initial Available Chlorine Concentration on the NMHC Removal

Table 2 shows experimental data for the oxidation scrubbing liquid and those of the calculated specific Cl_2 consumption for the 8 test runs. As shown in the table, initial available chlorine concentrations were varied from 44 to 375 mg/L with adjustment of pH and the initial pH varying from 6.5 to 7.0. NMHC in the influent gas varied from 3.13 to 25.3 ppm (expressed as methane equivalent). Table 3 shows experimental data for the reduction scrubbing liquid and data on the calculated fractional Cl_2 purged from the oxidation scrubbing liquid.

In Tables 2 and 3, the calculated data on the chlorine consumption need to be explained. Chlorine may be consumed due to the oxidation of the influent NMHC and to being purged from the oxidation liquid to the effluent gas. The mass of Cl_2 consumption can be estimated as follows:

$$\text{Mass of } Cl_2 \text{ consumed (mg)} = \Delta[Cl_2]_L \text{ mg/L} \times 0.60 \text{ L} \quad (2)$$

where $\Delta[Cl_2]_L$ is the difference of available Cl_2 concentrations in the oxidation liquid at the initial and end of the absorption test and 0.60 L is the oxidation liquid volume.

Chlorine being purged from the oxidation liquid may account for a significant part of the consumption. The purged mass can be estimated as follows:

$$\text{Mass of } Cl_2 \text{ purged (mg)} = [Cl_2]_G \text{ (ppm)} \times [71 \text{ (mg/m}^3)/ (24.5 \text{ ppm})] \times V \text{ (m}^3) \quad (3)$$

where $[Cl_2]_G$ is the average Cl_2 concentration in the effluent gas from the oxidation liquid at the initial and end of the absorption test, V is the total test gas volume (evaluated at
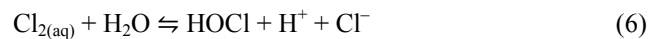
$25 \pm 2°C$) introduced to the scrubbing system in the test run. The quotient "71 (mg/m^3)/(24.5 ppm)" converts volumetric concentration (ppm) to mass-volume concentration (mg/m^3) for gaseous chlorine at the condition of atmospheric pressure and 25°C.

As shown in Table 3, the average Cl_2 concentration $[Cl_2]_G$ in the effluent gas from the oxidation liquid is equivalent to that in the influent gas to the reduction liquid. $[Cl_2]_G$ ranged from 2.3–11.4 ppm as shown in the table. The values were much higher than those calculated from partition of chlorine in gas and liquid water as described by the Henry's law:

$$P = C/H \quad (4)$$

where P (bar) is the equilibrium partial pressure of chlorine in the gas phase, C (mol/L) is the equilibrium mol concentration of chlorine in the aqueous phase, and H (mol/L/bar) is the Henry's law constant. At 25°C, H is 0.095 mol/L/bar as given by Lide and Frederikse (1995) and 0.061 mol/L/bar by Wagman *et al.* (1982).

For estimation of P in the gas phase in equilibrium with the available chlorine concentration in the aqueous phase, consider the following equations:

$$Cl_{2(g)} \leftrightarrows Cl_{2(aq)} \quad (5)$$

$$Cl_{2(aq)} + H_2O \leftrightarrows HOCl + H^+ + Cl^- \quad (6)$$

$$HOCl \leftrightarrows H^+ + OCl^- \quad (7)$$

The equilibrium constants of the above equations at 25°C are:

$$H = C/P = 0.061 \text{ or } 0.095 \text{ M/bar} \quad (8)$$

Table 2. Experimental data for the oxidation scrubbing liquid and data on the NMHC removed.

Run No.	V (L) [1]	Oxidation scrubbing liquid				Gas NMHC (mg/m^3)		NMHC removed (%) [8]
		Available Cl_2 (mg/L)		pH				
		Initial [2]	Final [3]	Initial [4]	Final [5]	Influent [6]	Effluent [7]	
1	22	44	39	6.95	6.97	9.65	2.09	78.3
2	40	90	80	7.05	7.00	5.19	0.84	83.8
3	24	185	165	7.03	7.02	3.13	0.64	79.6
4	22	375	319	7.06	7.02	7.49	0.42	94.4
5	15	55	53	6.54	6.59	25.27	4.09	83.8
6	10	92	90	6.50	6.56	10.11	3.07	69.6
7	10	188	172	6.57	6.72	15.57	1.88	87.9
8	10	360	360	6.57	6.70	14.83	1.11	92.5

[1] Total test gas volume (evaluated at $25 \pm 2°C$) introduced to the scrubbing system in the test run.
[2] Available Cl_2 in the oxidation liquid before the absorption test.
[3] Available Cl_2 in the oxidation liquid after the absorption test.
[4] pH of the oxidation liquid before the absorption test.
[5] pH of the oxidation liquid after the absorption test.
[6] Time-averaged NMHC concentration of the influent gas to the oxidation scrubbing liquid.
[7] Time-averaged NMHC concentration of the effluent gas from the oxidation scrubbing liquid.
[8] NMHC removed (%) = $(C_{in} - C_{out})/C_{in} \times 100\%$.

Table 3. Experimental data for the reduction scrubbing liquid and data on the calculated fractional Cl_2 purged from the oxidation scrubbing liquid.

| Run No. | V [1] | Reduction scrubbing liquid | | | | Cl_2 purged (mg) [6] | Cl_2 consumed (mg) [7] | Fraction Cl_2 purged [8] |
| | | Gas Cl_2 (ppm) | | pH | | | | |
		Influent [2]	Effluent [3]	Initial [4]	Final [5]			
1	22	2.3	0.3	12.3	12.2	0.147	2.40	0.061
2	40	5.4	0.2	12.3	12.2	0.626	6.00	0.104
3	24	10.3	0.3	12.3	12.2	0.716	12.0	0.060
4	22	7.1	0.2	12.3	12.2	0.453	33.6	0.013
5	15	5.4	0.3	12.0	11.8	0.235	1.20	0.196
6	10	4.3	0.2	12.2	12.1	0.125	1.20	0.104
7	10	3.4	0.2	12.1	12.1	0.099	9.60	0.010
8	10	11.4	0.3	12.1	12.1	0.330	0.00	-

[1] Total test gas volume (evaluated at $25 \pm 2°C$) introduced to the scrubbing system in the test run.
[2] Average Cl_2 concentration in the effluent gas from the oxidation liquid at the initial and end of the oxidation test.
[3] Average Cl_2 concentration in the effluent gas from the reduction liquid at the initial and end of the reduction test.
[4] pH of the reduction liquid before the absorption test.
[5] pH of the reduction liquid after the absorption test.
[6] Mass of Cl_2 being purged from the oxidation liquid, as calculated by Eq. (3).
[7] Mass of Cl_2 consumed in the in the test run, as calculated by Eq. (2).
[8] Fraction Cl_2 purged as calculated by dividing data [6] by [7].

$$K_H = [HOCl][H^+][Cl^-]/[Cl_{2(aq)}] = 4.2 \times 10^{-4} \qquad (9)$$

$$K_A = [H^+][OCl^-]/[HOCl] = 3.0 \times 10^{-8} \qquad (10)$$

where K_H is the hydrolysis constant of chlorine as given by Greenwood and Earnshaw (1997), and K_A is the ionization constant of HOCl as given by Morris (1966).

According to the equations, P were estimated to be 3.00×10^{-9} bar (3.00×10^{-3} ppm) and 3.79×10^{-8} bar (3.79×10^{-2} ppm) with a total available chlorine concentration ($[Cl_{2(aq)}] + [HOCl] + [OCl^-]$) of 213 mg/L ($10^{-3}$ M) at liquid pH of 7.0 and 6.0, respectively, at 25°C. With a total available chlorine concentration of 2,130 mg/L (10^{-2} M) at pH 6, P was estimated to be 3.79×10^{-6} bar (3.79 ppm) at 25°C. The calculated P values imply that chlorine in the vented gas from the oxidation liquid with an available chlorine concentration of as high as 2,130 mg/L at pH 6 is around 3.79 ppm. The result indicates that chlorine loss from the vented gas should be rather limited. The much higher $[Cl_2]_G$ (2.3–11.4 ppm) in the vented gas from the oxidation liquor might be due to the mist entrained by the bubbles.

According to data listed in Tables 2 and 3, Fig. 4 shows variations of NMHC removal efficiency with the initial available chlorine concentration ($[Cl_2]_o$) of the oxidation scrubbing solution. Results show optimal initial available chlorine concentrations of around 300–370 mg/L for achieving a NMHC removal of around 90%. As shown in Table 3, expect Run. No. 5, the fractional loss of Cl_2 from the purged gas was less than 10.4% and oxidation of the influent NMHC with the $[Cl_2]_o$ kept in the range of 300–370 mg/L is adequate for practical applications. Data shown in Table 3 also show that conditions with pH in the range of 12.0–12.3 and 0.35% H_2O_2 in the reduction liquid, the effluent gas from the liquid had no detectable chlorine and other odors.
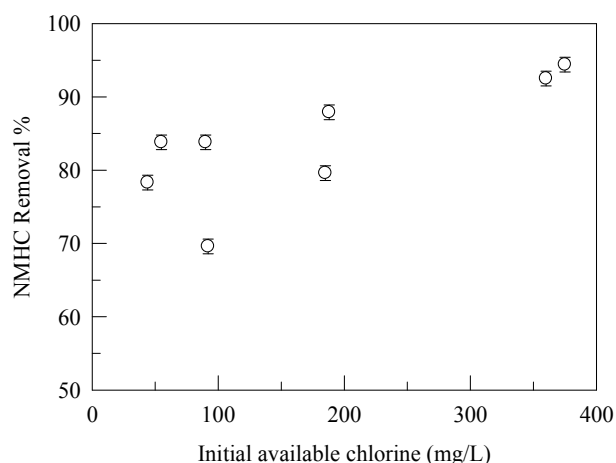
Fig. 4. Variations of NMHC removal efficiency with the initial available chlorine concentration ($[Cl_2]_o$) of the oxidative scrubbing solution (($[Cl_2]_o$ = 50–100 mg/L, average NHHC removal = 79%; $[Cl_2]_o$ = 186 mg/L, average NHHC removal = 84%; $[Cl_2]_o$ = 370 mg/L, average NHHC removal = 93%).

Table 4 shows calculated data for obtaining the mass consumption Cl_2 for the oxidation of unit mass of the NMHC. In Table 4, the total mass of NMHC removed from the gas in a test run can be estimated by the following equation:

$$\text{Mass of NMHC removed (mg)} = \Delta[NMHC]_G \text{ (ppm)} \times 16 \text{ (mg/m}^3) \times (24.5 \text{ ppm})^{-1} \times V \text{ (m}^3) \qquad (11)$$

where, $\Delta[NMHC]_G$ is the average of the difference of NMHC concentrations in the influent and effluent gas at the initial

Table 4. Calculated data for the mass of Cl_2 consumption and mass of NMHC removal in each run.

Run No.	NMHC removed (mg) [1]	Cl_2 consumption for the oxidation of the NMHC (mg) [2]
1	0.167	2.25
2	0.174	5.37
3	0.060	11.3
4	0.156	33.1
5	0.318	0.965
6	0.070	1.08
7	0.137	9.50
8	0.137	0
Average [3]	0.154	5.08

[1] NMHC removed (mg) = Gas NMHC removed (mg/m^3) × total test gas volume introduced to the scrubbing system in the test run (m^3, evaluated at 25 ± 2°C).
[2] Cl_2 consumption (mg) for the oxidation of the NMHC = Cl_2 consumed (mg) – Cl_2 purged (mg).
[3] Data of Run No. 4 and 8 not included for obtaining the average value.

and end of the absorption test. The quotient "16 (mg/m^3)/ (24.5 ppm)" converts volumetric concentration (ppm) of gaseous NMHC (expressed as methane equivalent) to mass-volume concentration (mg/m^3) for the gas at the condition of atmospheric pressure and 25°C. The total mass of Cl_2 consumption for the oxidation of the removed NMHC from the gas in a test run can be estimated by subtracting the mass of Cl_2 purged from the oxidation solution by the mass of Cl_2 consumed in a run. By the data, Fig. 5 shows a correlation between the mass of Cl_2 consumption and mass of NMHC removal for the six runs. It seems that Cl_2 consumption decreased approximately with increasing mass of NMHC removal. On an average, as shown in Table 4, 5.08 mg Cl_2 was consumed for the removal of 0.154 mg NMHC, or 33 mg Cl_2 consumed for the removal of 1.0 mg NMHC.

GC-MSD Examination

GC-MSD examination results (Table 5) indicate that acrolein, acetone, benzene, ethyl benzene, styrene and α-methyl styrene were detected in the untreated test gas and some of them could be removed by the oxidation liquid.

Benzene and ethyl benzene were not effectively removed due possibly to that both have a lower water solubility or higher Henry's law constant (dimensionless Henry's law constant $m = y/x$ = gaseous concentration (mg/m^3)/aqueous concentration (mg/m^3) = 0.23 at 25°C) than styrene (m = 0.109) (Eastem Research Group, 1997).

Table 5 also shows that the influent styrene was 1.06 ppm (4.5 mg/m^3 at 25°C) and the total mass of the influent
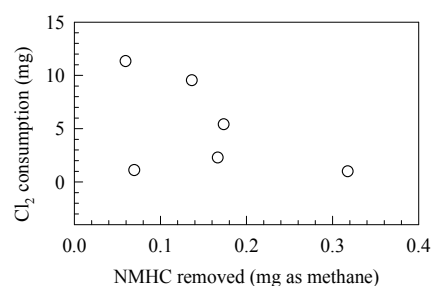
Fig. 5. Correlation between the mass of Cl_2 consumption and mass of NMHC removal for the six runs.

styrene for 30 minutes was 0.135 mg (4.5 mg/m^3 × 1 L/min × 0.001 m^3/L × 30 min = 0.135 mg). According to the Henry's law, the saturated concentration of styrene in water was around 0.041 mg/L when equilibrium with a styrene concentration of 4.5 mg/m^3 in the gas phase. The oxidation liquid had only a maximum capacity of absorbing 0.0246 mg of styrene (0.041 mg/L × 0.6 L = 0.0246 mg). Accordingly, most of the influent styrene (0.135 mg) had been oxidized rather than absorbed. The most possible one of the oxidation products of styrene by hypochlorous acid may be styrene oxide (Liu *et al.*, 2002).

Olfactory Test

According to the GC-MSD data (Table 5) for the influent and effluent gases to and from the oxidation liquid, the odor threshold of styrene is 35 ppb and the odor concentration of

Table 5. GC-MSD data for the influent and effluent gases to and from the oxidation liquid.

Component	Odor threshold (ppb)	Concentration (ppb)		Removal %	Odor concentration	
		Influent	Effluent		Influent	Effluent
Acrolein	36	18.6	ND	100	0.52	ND
Acetone	42,000	197	1.1	99.0	0.0047	0.00003
Benzene and ethyl benzene	160	210	168	19.9	1.3	1.1
Styrene	35	1060	195	81.6	30	5.6
α-Methyl styrene	250	11	ND	100	0.044	ND

Odor thresholds refer to Cheremisinoff, 1992.
ND: Not detectable.
Odor concentration (dimensionless): Concentration ÷ Odor threshold.

the influent gas was estimated to be 30 which could be easily detected by olfactory sense. The indicator of odor in this work is styrene

Take Run 8 as an example, odor intensities of the influent gas could be reduced from 3,090 (expressed as dilutions to threshold) to 55. Pungent burnt plastic odor in the test gas was almost completely removed. The odor intensity (55) of the scrubbed gas meets the regulation of less than 1,000 for exhaust gas from an emission pipe with a height of lower than 18 m above ground, as set by the EPA of Taiwan.

Chlorine Consumption for the NMHC Removal

In general, practical applications need data on Cl_2 consumption for treating unit volume of the influent gas to estimate the chemical consumption cost. The volumetric Cl_2 consumption can be estimated by the equation:

Volumetric Cl_2 consumption (kg Cl_2 (1,000 m^3)$^{-1}$ influent gas) = Specific Cl_2 consumption (kg Cl_2 (kg NMHC removal)$^{-1}$) × Influent gas NMHC (ppm as methane) × NMHC removal fraction × 16 (mg/m^3) × (24.5 ppm)$^{-1}$ × 1,000 Nm^3 × 10^{-6} kg/mg (12)

Estimation of Chemical Requirements and Costs

Solutions of sodium hypochlorite solution, hydrogen peroxide, and sodium hydroxide are needed to add to the solutions of the 2-stage chemical scrubbers used in the present study.

Take an emitted gas with 10 ppm NMHC and a NMHC removal of 90% as an example, the volumetric Cl_2 consumption can be estimated to be 1.62 kg 12% chlorine bleaching solution for treating 1,000 m^3 of the gas. According to data shown in Table 4, effluent gas from the oxidation liquid (influent gas to the reduction liquid) has a maximum chlorine of 11.4 ppm, the required chemicals for reduction of the chlorine introduced to the reduction liquid and neutralization of the reduced product (HCl) can be calculated by following the stoichiometry of Eq. (1). Taking 1,000 Nm^3 of the influent gas with 11.4 ppm chlorine to the reduction liquid as a base, mass of Cl_2 = 4.65 × 10^{-4} kmol, mass of 35% H_2O_2 = 0.0452 kg, and mass of 45% NaOH = 0.0372 kg.

Table 6 lists the required amount of chemicals for treating 1,000 m^3 of the emitted melting gas. Based on the local costs for the chemicals, around USD 0.32 are required. The cost analysis in Table 6 addressed only on the required chemical costs for treating 10^3 m^3 of the melting gas. Fixed cost for an application of the technique to treat a full-scale effluent gas should consider sizing of scrubbers for absorbing the pollutants from the gas. The cost depends on the gas flow rate and the required instruments for process control.

Secondary Pollution Control

Replacement of the scrubbing liquors may be once per day or a few days, depending on the pollutant contents in the gas or liquors. The replacement can also be continuously following the continuous operation mode of the hot-melting operations. The chemicals employed in this study including NaOCl, NaOH and H_2O_2 are all strong oxidizing

Table 6. Requirement of chemicals and the costs for treating 1,000 m^3 emitted melting gas.

Chemical	Amount (kg)	Unit cost (USD/kg)	Cost (USD/1,000 m^3)
Bleaching solution (12% Cl_2)	1.62	0.167	0.271
Hydrogen peroxide (35%)	0.0452	0.500	0.0226
Sodium hydroxide (45%)	0.0827	0.333	0.0275
Total			0.321

solution. Release of these chemical solutions into wastewater treatment plant or aqueous environment may lead to an adverse effect on the biological process of wastewater treatment plant or the ecosystem. Therefore, these chemicals should be appropriately treated before they are discharged into aqueous system.

It is suggested that the effluent scrubbing solutions from the oxidation scrubber (mainly HOCl) and the reduction one (mainly H_2O_2 + NaOH) should be introduced into a mixing chamber and reacted for a definite time for reducing the possible adverse effects. The associated reaction in the mixing chamber is HOCl + H_2O_2 + NaOH → NaCl + 2H_2O + O_2. A reducing agent (e.g, NaHSO$_3$) should be added to the effluent from the chamber to reduce either excess free chlorine (OCl$^-$ and HOCl) or H_2O_2 to either chloride (OCl$^-$ + NaHSO$_3$ → NaCl + HSO$_4^-$) or H_2O (H_2O_2 + NaHSO$_3$ → H_2O + NaHSO$_4$).

CONCLUSIONS

This study used a small-scale two-stage scrubbing method in a laboratory setting to remove odors and VOCs from PS melt exhaust gas. The following conclusions can be drawn:
1. By the oxidation solution with an available chlorine of 300–370 mg/L at an unadjusted pH (6.5 to 7.0), and reduction solution with pH > 12.0 and 0.35 % H_2O_2, around 90% of the hot-melt VOCs in the range of 3.2–55.5 ppm (expressed as methane equivalent) could be removed. Effluent gas from the system had no detectable chlorine and other odors.
2. VOCs in the hot melt exhaust consist mainly of acrolein, acetone, benzene, ethyl benzene, styrene and α-methyl styrene. The two-stage chemical scrubbing process removed 82–100% of the detected VOCs except benzene ethyl benzene.
3. It requires around 1.62, 0.0452, and 0.0827 kg NaOCl solution (12% available Cl_2), H_2O_2 solution (35% H_2O_2), and NaOH solution (45% NaOH), respectively, for scrubbing 1,000 m^3 of the exhaust gas with 10 ppm NMHC (expressed as methane equivalent). The chemicals cost a total of approximately USD 0.32.

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