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The trapping of indoor air contaminants

Invited Paper

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Abstract: The removal of indoor air contaminants by reactivity with air filters coated with reagents has been found to be effective for aldehydes, acidic and basic vapours as well as isocyanates Coatings of polymeric amines were used for formaldehyde trapping as well as for the removal of acidic vapours and for the removal of isocyanates. The addition of glycerol as a plasticizer for the coating can also be an effective reagent.

Keywords: *Indoor air • Aldehydes • Acids • Bases • Isocyanates*

1. Introduction

Indoor air quality has always been a problem and of concern in the workplace. During the energy crunch of the mid 70s this problem was extended to the home where the conservation of energy due to the rising prices meant that windows were kept shut and the exchange of indoor air was significantly reduced. The problem reached the public in Canada where homeowners were financially encouraged to insulate their older homes using urea-formaldehyde foam insulation, (UFFI) that could be injected into the empty outdoor wall cavities. Improper formulation and foam instability led to the release of formaldehyde into the houses. This resulted in an epidemic of sick people who were now financially helped to remove the UFFI [1-4].

A simple solution which appeared too late for most homeowners was developed [5-7] and patented by Gesser [8-10] who showed that it was possible to remove most of the indoor formaldehyde by treating the furnace filter, through which the indoor air was circulated by the furnace fan motor. The filter coating chosen was a polymeric amine that was plasticized with glycerol to keep the coating from drying to a solid and which would allow for diffusion within the coated layer. It was also shown that a box fan with the coated filter attached could be equally effective in removing indoor pollutants by reaction with the filter when a forced air furnace was not available. Much work has been done since then to improve the quality of indoor air. Some attention has been focused on the Sick Building Syndrome (SBS) and related effects [11-13]. Other reviews [14,15] have concentrated primarily on formaldehyde and its removal. Marutzky [16] has shown how indoor formaldehyde concentrations can be reduced by four processes: 1) Enlarging ventilation, 2) Removing the source of emission, 3) Sealing off the emitting source, and 4) Chemical treatment with ammonia. A fifth method [17] can include the destruction of the formaldehyde by passing the air through a solution of $KMnO_4/H_2SO_4$. These methods may seem simple but in practice they are not suitable for the home.

Other methods have been developed, and supported by the National Aeronautics and Space Administration (NASA), that include the ability of certain plants to absorb indoor VOC contaminants that include formaldehyde [18-21], benzene [22] as well as the other aromatic hydrocarbons [23] and other volatile organic vapours, VOCs [24-28] expected to be present in spacecrafts. The photocatalytic oxidation (PCO) of organic pollutants has been extensively studied using primarily TiO_2 as the photocatalyst. This is an inefficient process because the titanium oxide is usually of small area and not fully transparent. However some interesting results have been obtained [29-33]. Gesser has reported on a porous amorphous titania glass that is transparent down

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to 450 nm and which should be an excellent photocatalyst since it can transmit the UV to dissociate the water molecule [34]. Other photocatalytic systems devoted to environmental clean-up using model compounds such as acetone [35], toluene [36] and toluene and nitric oxide [37] have been reported. The purification of air by filtration [38], and the use of active surfaces to adsorb the volatile contaminants have been reported for fly ash [39]. Active carbon impregnated High Efficiency Particulate Air (HEPA) filters [40] or active carbon fibers [41] and carbon fabrics [42] have been recently reported to purify the indoor air to varying degrees from model contaminants. Patents have been issued in which the coatings on a filter had been tailored to the contaminant to be removed [43]. These included odours [44], and cigarette smoke [45]. With the introduction of space travel and the closed spacecraft during the long journeys anticipated the control of indoor air contaminants has been extensively studied by NASA [18].

The common air circulating system in homes and commercial building utilized for heating and cooling are usually fitted with filters to remove particulate matter. Such filters are ideally suited for removing indoor contaminants by means of a reactive coating that can be added to the filters. We have chosen, for convenience, vapours that represent an acid (SO_2), a base (NH_3), an aldehyde (CH_3CHO) and toluene diisocyanate as representatives of the class of compounds that can interact with the filter coating. We now report on the mechanism of such systems previously studied and show how diffusion within the coated layer extends the usefulness of the trapping system. We shall also show how the glycerol used to keep the coated layer in a mobile liquid phase can participate with amines in a reactive mode to remove isocyanates from indoor air.

2. Experimental Procedure

2.1. Indoor air

The apparatus used to generate some of the test gases and to monitor their flow and analysis is shown in Fig. 1. Purified air was passed through a humidifier before being mixed with the test vapours and entered the test chamber containing the treated filter (14 cm diameter, 10 mm thick) for a single pass. The concentration of the test vapours were monitored continuously with the Miran Infrared Analyzer. The 3M High Air Flow (HAF) filters were coated with either a polymeric basic amine, polyethylenimine (PEI), (FX-A) to trap acidic vapours as well as aldehydes and ketones or a polymeric acid, polyacrylic acid (FX-B) to trap basic vapours. The coatings also included glycerol as the plasticizer that was intended to keep the coating fluid and permit diffusion within the coated layer. The coated filters were dehydrated at 90°C for 60 min and allowed to come to room temperature before being inserted into the test chamber after a uniform measured flow of the test vapour was achieved and the 100% level established. The treatment data are shown in Table 1 where the results indicate that the drying was not done for the Sample C (acetaldehyde). It remains to determine if such drying treatment is needed.

Off-gassing of the challenge compounds from the filters was evaluated by turning the challenge gas off after 10 min of testing, allowing clean air to pass through the filter, and recording the downstream concentration.

2.2. Isocyanate removal

The flow system used was similar to that previously reported [6,7]. Air flow from a compressed air cylinder was controlled by means of a pressure regulator and needle valve and passed through a dryer, a flow meter and into a sample of toluene diisocyanate (TDI) controlled at a constant temperature. The air flow then passed into a glass chamber containing reticulated open cell polyurethane foam plugs (OCPUF) coated with a polyethylenimine/glycerol mixture. The OCPUF was 7 cm in diameter and 2 cm thick. The air flow was 17.5 L min^{-1} which corresponded to a linear velocity of 4.5 m min^{-1}. The TDI was determined by the NIOSH method P & CAM 141 that involved bubbling the TDI into an acidic solution converting the isocyanate into an amine that was reacted with nitrite to form the diazo compound. A coloured solution was formed when this was reacted with NNED {N-1(-Naphthyl)-ethylenediamine)}. The coloured solution was determined quantitatively by absorption at 550 nm from a calibration graph. At a reservoir temperature of 48° C the concentration of TDI in the air stream was determined to be 0.03 mg m^{-3}.

3. Results and Discussions

3.1. Indoor air

The single pass trapping efficiency of FX-A filters is given in Fig. 2 for SO_2 at 29 ppm and acetaldehyde at 52 ppm and for ammonia at 51 ppm by FX-B. The trapping efficiency seems to vary significantly from one substance to another. A test for off-gassing of a loaded filter is shown in Figs. 3, 4 and 5 for the three gases. Some off-gassing is observer by the slow return of the concentration to baseline as indicated for the ammonia and acetaldehyde but not for SO_2.

Since the FX solutions contain glycerol, a viscous liquid, it was anticipated that allowing a loaded filter to

Table 1. FX treatment of HAF samples

Sample	Treatment Solution	Diameter of HAF sample	Mass of HAF sample (g)	Wet sample mass (g)	Mass of treatment solution after drying (g)
NH_3 (A)	FX-A	140 mm	16.61	20.52	5.79
SO_2 (B)	FX-B	140 mm	15.74	19.11	4.90
CH_3CHO (C)	FX-A	142 mm	16.95	19.12	not dried

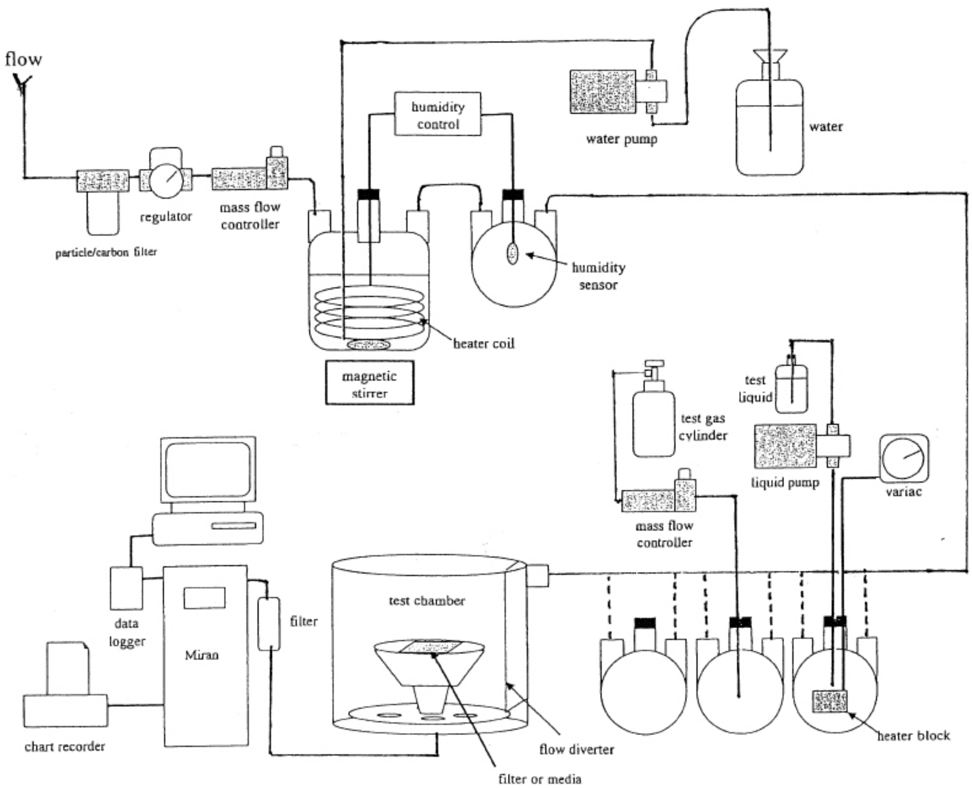

Figure 1. Test apparatus for "Indoor Air" part.

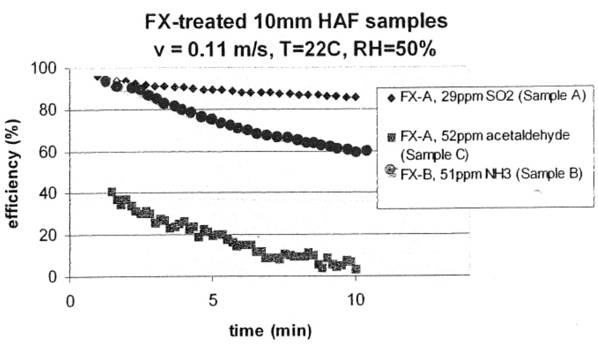

Figure 2. Efficiency of 10 mm HAF filter coated with FX solutions.

age may "recharge" the filter as the active chemicals diffuse to the surface of the solution, thus becoming available for reaction. This effect was tested at two timescales by:

1. Allowing clean air to pass through loaded samples for 2 to 4 minutes and retesting. Any observed "recharging" would be due to a combination of the challenge analyte off-gassing from the sample and diffusion of the active compounds in the glycerol.

2. Sealing samples in plastic bags, allowing them to sit for 3 to 6 days, and retesting.

These results are shown in Figs. 6 and 7 and indicate significantly greater "recharging" with time.

The effect of using glycerol in the acid or base treatment of HAF was evaluated by studying the single-pass efficiency and reaction completeness for monomeric acid or base treated HAF. The results are shown in Fig. 8 for SO_2 and Fig. 9 for NH_3. The role of each of the components, acid or base, glycerol, and water become evident Integrating the areas under the curves show that significantly higher single-pass efficiencies and reaction completeness (over 75%) is observed when glycerol is added to the treatment solutions. The possible loss of HCl by evaporation from

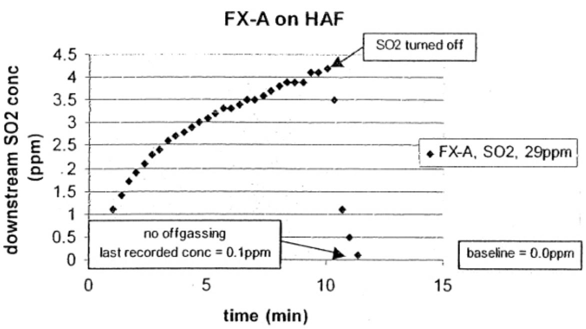

Figure 3. Evidence of minimal off-gassing of SO_2 from FX-A sample (Sample A).

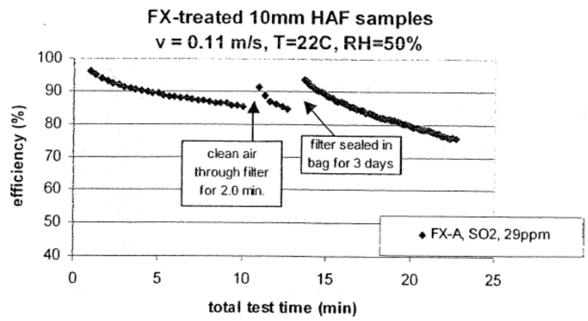

Figure 6. "Recharging" of FX-A sample (Sample A).

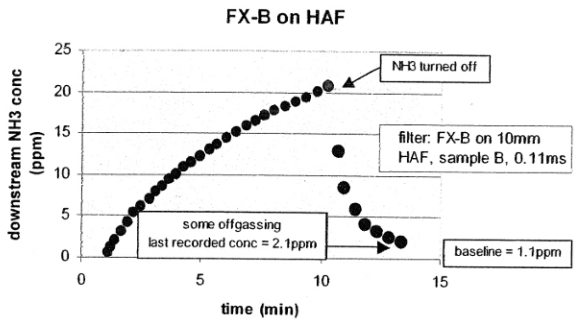

Figure 4. Evidence of some off-gassing of NH_3 from FX-B sample (Sample B).

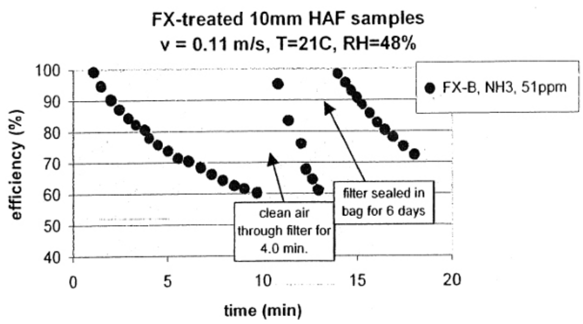

Figure 7. "Recharging" of FX-B sample (Sample B).

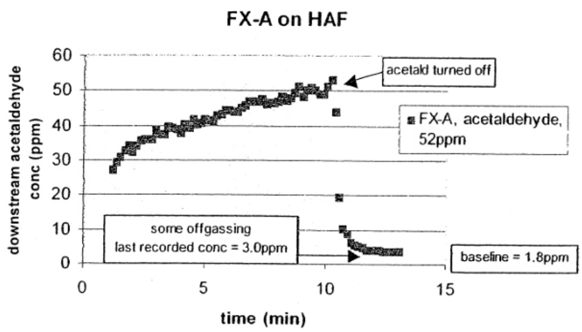

Figure 5. Evidence of some off-gassing of acetaldehyde from FX-A sample (Sample C).

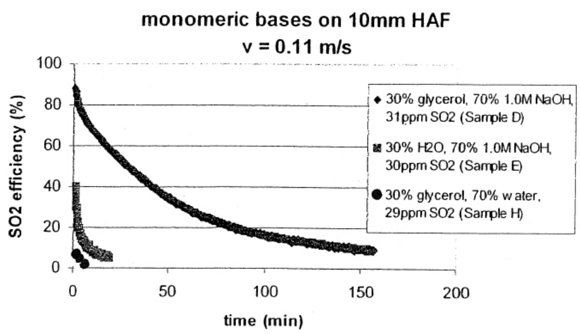

Figure 8. Sulphur dioxide trapping efficiency of base-treated HAF.

the dried sample could be avoided by the use of the less volatile sulphuric acid in future studies. It was also noted that glycerol did not react significantly with the challenge analytes. The small efficiencies shown by the glycerol solutions is probably due to absorption of the analytes by glycerol.

Off-gassing of the challenge compounds from the filters that were treated with monomeric acid or base was evaluated by turning the challenge gas off after testing and allowing clean air to pass through the filter while recording the downstream concentration. These results are shown in Figs. 10 and 11.

Each filter (with the exception of Sample E, (water + NaOH) which did not remove much analyte) showed some off-gassing. Since the FX samples were not fully loaded with analyte, it is difficult to determine if a higher degree of off-gassing was observed for the samples treated with monomeric acids (Figs. 10 and 11) *vs.* the samples loaded with polymeric acids and bases (Figs. 3 and 4).

The uptake of water by FX-A, FX-B and glycerol solutions was evaluated by placing a small amount (<35 g) of solution in the bottom of a 120×90 mm aluminum pan, drying the solution at 75ºC for 39 h, storing the solutions in an environment chamber at 25ºC and 50% RH, and weighing periodically. Water uptake was studied because the presence of water affects the diffusion of acid/base treatments, and thus affects the reaction kinetics and reaction completeness. The results of this study are shown in Fig. 12. It appears that water saturation is approached within a day or two and consideration for this must be taken into account.

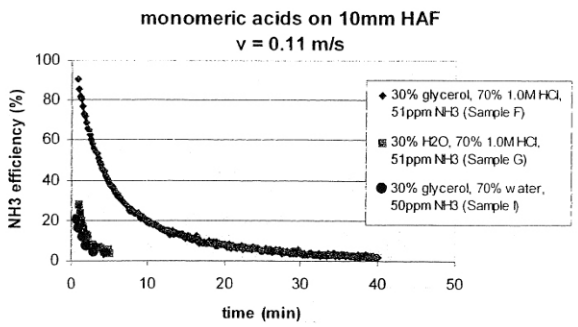

Figure 9. Ammonia trapping efficiency of acid-treated HAF.

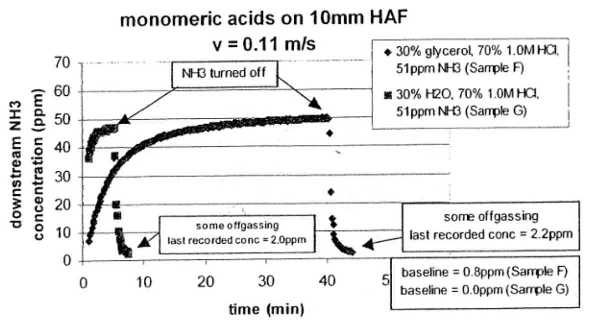

Figure 11. Off-gassing of ammonia from acid treated HAF.

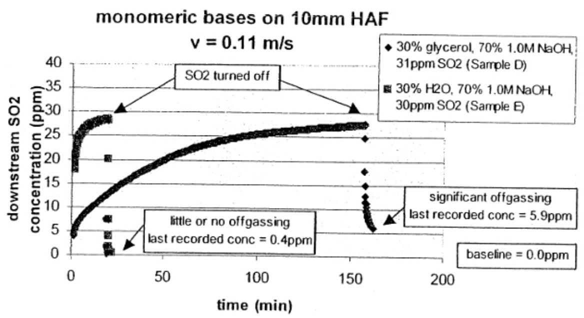

Figure 10. Off-gassing of sulphur dioxide from base treated HAF.

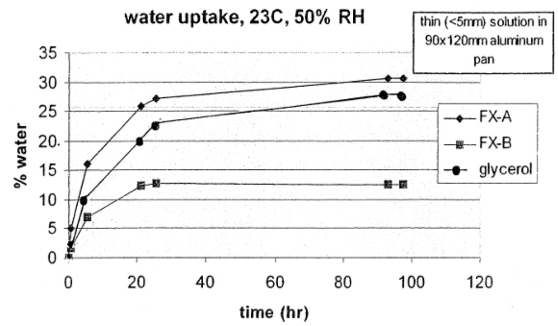

Figure 12. Uptake of water at 25°C and 50% RH by different coating solutions.

3.2. Isocyanate removal

The concentration of isocyanate in the work place was determined to be 0.028 ppm before the filter was installed. After the air was circulated through the coated filter the concentration of the isocyanate in the workplace was determined to be <0.005 ppm. It is possible that both the PEI as well as the glycerol on the filter remove the TDI. This was confirmed by tests with glycerol but it was not possible to compare its efficiency with TDI at this time.

4. Conclusion

A reactive coating on filters have been shown to be effective when plasticized with an "inert" low volatile water soluble liquid such as glycerol. A plasticized polymeric acid was shown to chemically trap basic vapours and basic polymeric coatings (such as $R\text{-}NH_2$) trapped acidic vapours as well as aldehydes. When the flow of toxic vapours are stopped or reduced the diffusion of the reaction products from the air-liquid interface and its replenishment by fresh reactant effectively revitalizes the filter and permits additional trapping capacity. The role of the two components, reactant and glycerol (water is removed and only used to form the initial solution) the "solvent" allows full reactant capacity.

In general, the reactive coating on an air filter or support presents a new and interesting alternative to the active surface trapping of gases on large surface area solids such as carbon, silica gel and molecular sieves. The adsorption process is handicapped by the general nature of the process and the interference of water vapour or higher temperatures that limit the adsorption process for the targeted gases and vapours.

The specific reaction process needed can be tailor made (within limits) for the targeted substances. The recent appearance of several patents on acidic and basic coatings for filters to produce clean air illustrated this feature. The strength of such systems lies in the specificity of the coatings. The use of multilayered filters for reactions with different contaminants has already been proposed [43]. It remains to be seen how successful such system are to maintain a 'clean' indoor environment.

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References

[1] Indoor Pollutants (National Academy Press, Washington D.C., 1981)
[2] J.F. Walker, Formaldehyde (Reinhold Publ., New York, 1964)
[3] V. Turoski (Ed.), Formaldehyde, Analytical Chem. & Toxicology, Advances in Chemistry Series, No. 210 (American Chem Soc., Washington, 1985)
[4] L. Tataryn, Formaldehyde on Trial (J. Lorimor & Co., Toronto, 1983)
[5] H.D. Gesser, Environ. Intern. 10, 305 (1984)
[6] H.D. Gesser, S. Fu, Environ. Sci. & Technol. 24, 495 (1990)
[7] H.D. Gesser, I.E. Gesser, P. Wong, Environ. Intern. 18, 463 (1992)
[8] H.D. Gesser, Abatement of Indoor Pollutants, US Patent # 4547359, Oct. 15, 1985
[9] H.D. Gesser, The Abatement of Indoor Formaldehyde Vapor and Other Indoor Gaseous Pollutants, Can. Patent # 1241524, Sept. 6, 1988
[10] H.D. Gesser, The Removal of Aldehydes and Acidic Gases from Indoor Air, US Patent # 4892719, Jan. 9 1990
[11] A. Petrovitch, Umweltmedizin in Forschung und Praxis 1(3), 143 (1996)
[12] A.P. Jones, Atmospheric Environment 33(28), 4535 (1999)
[13] B.O. Brooks et al., J. Toxicology, Clinical Toxicology 29(3), 315 (1991)
[14] R. Chenier, Human and Ecological Risk Assessment 9(2), 483 (2003)
[15] R. G. Liteplo et al., Formaldehyde, Concise International Chemical Assessment Document 40(i-v), 1 (2002)
[16] R. Marutzky, Holz als Roh-und Werkstoff 47, 207 (1989)
[17] H. Tsutsumi et al., Yakugaku Zasshi 125(6), 517 (2005)
[18] B.C. Wolverton et al., Economic Botany 38(2), 224 (1984)
[19] T. Oyabu et al., Sensors and Actuators, B: Chemical B89(1-2), 131 (2003)
[20] K.J. Kim, D.W. Lee, Horticulture, Environment and Biotechnology 49(2), 132 (2008)
[21] K.J. Kim, H.D. Kim, Horticulture, Environment and Biotechnology 49(3), 155 (2008)
[22] R.L. Orwell et al., Water, Air & Soil Pollution 157(1-4), 193 (2004)
[23] M.H. Yoo et al., J. American Soc. for Horticultural Sci. 131(4), 542 (2006)
[24] T. Oyabu et al., Taiki Kankyo Gakaishi 36(6), 319 (2001)
[25] T. Oyabu et al., Chemical Sensors 16(A), 37 (2000)
[26] J.C. Andrew et al., Env. Sci. & Tech. 42(1), 289 (2008)
[27] R. A. Wood et al., J. Hort. Sci. & Biotech. 77(1), 120 (2002)
[28] B. Guieysse et al., Biotech. Advances 26(5), 398 (2008)
[29] Y-w. Lu et al., Beijing Gongye Daxue Xuebao 34(2), 184 (2008)
[30] H.C. Ao et al., Applied Catalysis, B: Enviro 54(1), 41 (2004)
[31] W. Sanongraj et al., J. Air & Waste Management Assoc. 57(9), 1112 (2007)
[32] P. Pichat et al., Catalysis Today 63(2-4), 363 (2000)
[33] N. Namiki et al., Kuki Seijo 36(4), 267 (1998)
[34] L. Kruczynski, H.D. Gesser, C.W. Turner, E.A. Speers, Nature 291, 399 (1981)
[35] G. Vincent et al., J. Photochem. & Photobio. A: Chem. 197, 177 (2008)
[36] N. Namiki et al., Kuki Seijo 35(4), 267 (1998)
[37] C. H. Ao et al., Chem. Engin. Sci. 60(1), 103 (2004)
[38] J. Gustavsson, Filtration-Separation 39, 14 (2002)
[39] S. Wang, X. Fan, Huabei Dianli Daxue Xuebao 332(6), 89, 96 (2005)
[40] W. Yin et al., Huanjing Wuran Zhili Jishu Yu Shebie 3(2), 53 (2002)
[41] R.G. Fuerman et al., Proceedings, Annual Meeting-Air & Waste Management Assoc. (1991), 84th(Vol 3) Paper 91/62.5, 11pp
[42] W. Davis et al., Separation Sci. & Tech. 36(5-6), 931 (2001)
[43] C. Lindhe, Multi-element air filter, US Patent # 5944676, Aug. 31, 1999
[44] D.L. Visioli, V. Brodie, Method for reducing odors in recycled plastics and compositions relating thereto, US. Patent # 5350788, Sept. 27, 1994
[45] R.R. Cohen, G.A. Luzio, Selective delivery and retention of aldehyde and nicotine by-products from cigarette smoke, US Patent # 5009239, Apr. 23, 1991