Control of Malodors using Ecosorb®
"A Natural Product"

Sulfur Dioxide, Hydrogen Sulfide, and Ammonia Mechanisms for their Removal

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ABSTRACT

Ecosorb removes many malodors, including sulfur dioxide, hydrogen sulfide and ammonia, from the environment. It is made up of a combination of essential oils consisting of an equilibrium of neutral organic compounds and organic buffers. Its pH ranges from 4.0 to 6.8.

Acidic malodors such as hydrogen sulfide and sulfur dioxide are removed by at least four mechanisms including solubility, oxidation/reduction, neutralization and addition across double bonds. Basic malodors such as ammonia and other amines are removed by at least three mechanisms including solubility, addition and neutralization. In all cases the final products consist of organic salts, newly formed organic compounds, very weak natural organic acids (those that were present in the original essential oil mixture), and malodors dissolved in the water/ oil mixture. Resulting organic compounds are frequently subjected to oxidation or reduction when in solution. In the case of sulfur dioxide and hydrogen sulfide these reactions result in the formation of free sulfur, or higher oxidation states including SO_2 and SO_3.

The removal efficiency is related to the interaction of the above-mentioned mechanisms, the atomizing efficiency (size and speed of droplets), humidity, temperature and reaction time.

INTRODUCTION

Malodors include acids, bases, and neutral compounds. Several of these are polar compounds and are water-soluble, others are non-polar and are soluble in other non-polar organic solvents. An example of using this solubility would be the scrubbing of ammonia gas from the atmosphere by misting it with water. Although this method can remove ammonia, the reaction is temperature dependent, reversible and not very efficient. The same statement could be made when applied to other soluble bases, soluble acids and even to some neutral compounds.

Some malodors, including sulfur compounds, can be oxidized by air when the compounds are in solution. During this process sulfur compounds can produce sulfur. This procedure is slow, not very efficient, and dependent on moisture content, temperature and mixing with air.

These mechanisms for odor removal can and will take place naturally, although inefficiently. Ecosorb contains a mixture of selected essential oils that can facilitate the efficient removal of many malodors.

Wilkinson and Zhang have broken the malodors down into four main groups which include bases, acids, neutrals and those that will not react with essential oils. A summary of this breakdown of 37 common malodors is shown in Table 1.

MALODORS			
	Group	**Reactions**	**Number of Compounds**
A.	Bases	React by acid/base mechanism 13 compounds plus CH_3S, TME, and DMEA	16
B.	Acids	(If they contain relatively small anions) 10 compounds including HCN and phenol, SO_2, C12 react by addition to a double bond and by neutralization.	10
C.	Neutrals	Includes styrene, CO, CO_2, acetaldehyde, ozone.	5
D.	Will not react	Possibly will not react with Ecosorb due to steric hindrance caused by large anion.	6
Total number of malodors			37

Table 1: Malodor Breakdown

The groups include the following malodors:

Group A: ammonia, butylamine, cadaverine, dibutylamine, diisopropylamine, dimethylethylamine, diphenyl sulfide, ethylamine, indole, methylamine, putrescine, pyridine, skatole, triethylamine, trimethylamine

Group B: ethyl mercaptan, hydrogen sulfide, methylmercaptan, propylmercaptan, hydrogen cyanide, chlorophenol, sulfur dioxide, phenol and sulfurous acid

Group C: acetaldehyde, chlorine, ozone, carbon monoxide, dioxide, and styrene

Group D: allyl mercaptan, amyl mercaptan, crotyl mercaptan, tert-butyl mercaptan, thiophenol (Contain large anions, which cause steric hindrance. These are not as common or as volatile as other compounds in Group A and B.)

Dr. Sylvain Savard, a chemist and Project Leader of the Center of Industrial Research for Quebec, Canada, prepared a report on “The Operating Principles of the Ecosorb System to Neutralize Odors”. He pointed out that Ecosorb is a combination of volatile essential oils that are selected for their ability to neutralize odors. The composition of these essential oils can vary because of many factors including:

1. Type of soil in which the plant is cultivated.
2. Time of year of harvest.
3. Part of the plant used.
4. Amount of water in the plant.
5. Amount of exposure to the sun during growth process.
6. Storage conditions before distillation.

The solution contains approximately 30 major chemical compounds, and numerous minor compounds (major and minor in terms of concentration).

Dr. Savard reports that the solution can react through three mechanisms including: Van der Waals Forces, Zwaardemaker pairing and chemical reactions. The solution is mixed with water and sprayed into small droplets, which are in the form of a mist or fog and remain airborne for long periods of time. These small droplets represent a large surface area, which are covered, or partially covered with a film of essential oils. The electrostatic charges on the droplet surface attract gas molecules. When in contact, removal by one of three mechanisms can occur. Sometimes this reaction is slow and other times it is fast. Once captured, the odor is gone. The droplets can cluster, increase in mass and condense.

Wilkinson and Zhang have studied possible chemical reactions between selected essential oils and hydrogen sulfide, sulfur dioxide and ammonia. The essential oils being studied contain three types of substances: weak organic acids, weak organic bases and neutral organic compounds. The acids and bases react and end up as a buffer solution. The oil mixture has a pH of approximately 4.5. When diluted the pH is approximately 6.0. This final buffer like solution is fairly stable, but can change pH with time depending on its environment and how well it is sealed from its environment. We have found the mixture of essential oils to have a pH between 4.0 and 6.0 in the concentrated form.

Based on experimental data already discussed, malodors can be classified into one of three categories: acids, bases and neutrals. Compounds such as hydrogen sulfide, sulfur dioxide, amine, ethyl amine, etc. are bases. Compounds such as styrene are neutral. Acids and bases will react with essential oil buffers in a normal acid/ base reaction forming organic salts and water. Many of these acids and some bases will react with the selected essential oils by addition across conjugated double bonds. This has been shown to be the case with hydrogen sulfide. The question of neutral compounds is still to be studied. Whatever the chemical mechanism or mechanisms involved, the amount of malodor reacting with the essential oils (the bulk kinetic prediction) is much less than the amount of malodor removed (recalculated amount) because of oils.

Previous reports have shown the particular mixture of oils to be very efficient in removing hydrogen sulfide, sulfur dioxide, ammonia, mercaptans, and alkylamines.

Dr. Davidovits of Boston College has studied the effects of pH and Van der Waals' forces on sulfur dioxide.[1] His work is extremely important. He shows how pH greatly affects the amount of sulfur dioxide that remains dissolved in water droplets. He observed as much as a 300% increase in the amount of sulfur dioxide that remained in water if the pH was increased from 3.0 to 6.0. He further concluded that the size and speed of the droplet greatly affected the effectiveness of removing sulfur dioxide from the atmosphere. He also discusses the tremendous effect pH has on the distribution constant of sulfur dioxide in water.

If the work of Dr. Savard, Carter Laboratories, Dr. Davidovits, Boston College and Dr. Wilkinson and Ms. Zhang, Delaware State University are combined, overall mechanisms for the effectiveness of selected essential oils in removing malodors from the environment develops.

Of primary importance in odor removal is the formation of very small droplets with an initial high velocity. This will ensure a large surface area and increased opportunity for collisions with gas molecules. If we are using only water, then the efficiency of removing gas molecules now depends on the solubility of each individual gas in water. The more soluble the gas, the more readily it will dissolve.

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[1] Davidovits, P. and Jayne, J.T., Department of Chemistry, Boston College, Chestnut Hill, Massachusetts and D.R. Worsnop, M.S. Zahniser, and C.E. Kolb of Aerodyne Research, Inc., Billerica, Massachusetts "Uptake of SO_2 (gas) by Aqueous Surfaces as a Function of pH: The Effect of Chemical Reaction at the Interface," Journal of Physical Chemistry 1990, 94, 6041-6048.

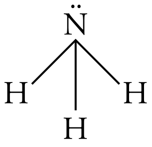
Once dissolved, the gas will begin to leave the droplet and establish an equilibrium (according to Henry's Law) between its concentration in the gas phase and its concentration in the aqueous phase. The pH of the droplet will greatly affect this solubility by a factor of as much as 300. Some gases are readily soluble, and others only slightly soluble. When selected essential oils are added to the mix the droplets are covered, or partially covered with a thin layer of essential oils. These oils attract most gases to the droplet surface where chemical reactions and pH effects come into play. The oils greatly influence the initial attraction of gas molecules, the pH greatly influences the solubility (gas uptake), and chemical reactions "irreversibly" remove some of the gas molecules by forming new, less volatile compounds. The change in the organic content of the droplet and a resulting change in its polarity all cause a large increase in the distribution constant between gas molecules in the vapor and aqueous phases. This increase indicates that more of the gas remains trapped in the aqueous layer than would normally be trapped at a given temperature.

EXPERIMENTAL RESULTS

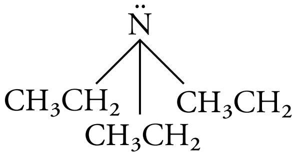
Mechanisms for Basic Malodors:

There are many amines that have been classified as malodors including triethylamine (TEA), and dimethylethylamine (DMEA), ammonia, and trimethylamine. These gaseous amines stimulate nerve endings in the nose and are irritants. They can lead to cell necrosis (cells swell and disintegrate) and increased permeability of the alveolar walls. They can cause flooding of the alveoli and produce a delayed pulmonary edema that may be fatal.

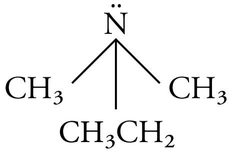
Ammonia is extremely soluble in water and will rapidly dissolve. The oils will have some effect on increasing the attraction of gas molecules to the droplet. A chemical reaction occurs between essential oil buffers and ammonia forming organic ammonium salts. Ammonia, which would normally easily leave the droplet, will now remain to a larger extent in the aqueous layer. This change in the distribution constant will keep the ammonia trapped in the water droplet until condensation occurs, affecting a very efficient removal of this gas from the environment. Since ammonia is a base, the oil mixture should be adjusted to a pH of approximately 4.0 to 6.2 to more effectively remove the gas. This would be true for any basic malodor (alkylamines, etc.). The pH of the essential oil mixture is typically in this range when used.



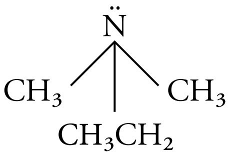
amonia
Figure 1



trimethylamine
Figure 2



triethylamine
Figure 3



dimethylethylamine
Figure 4

Ammonia (Fig. 1) is the most basic amine. It possesses a nitrogen atom containing a non-bonded electron pair. Its ability to donate this pair to other chemical compounds gives it the characteristic of a base. Notice that this is also true for trimethylamine (Fig. 2), as well as triethylamine (Fig. 3) and dimethylethylamine (Fig. 4).

Amines, being basic, will react with organic acids present in essential oils forming organic salts. The ease and rate of reaction is, in part, a function of the strength of the base. The strength of these bases can be measured by their equilibrium constant (Kb). The larger the value of Kb the more basic is the amine. Ammonia has a Kb of 1.8 x 10-5 (very weak), TME has a Kb of 6 x 10-1 (much stronger), DMEA has a Kb of approximately 2.3 (stronger than TME) and TEA has a Kb of 5.6 (slightly stronger than DMEA). Amines will readily react with the weak organic acids present in the selected essential oils. These weak organic acids are naturally occurring acids, which have proven not to be toxic or carcinogenic.[3,4]

DMEA	+	**H^+A^-**	=	**$DMEAH^+A^-$**
Amine	+	**Organic acid**	=	**An organic salt**
$(CH_3)_2(CH_2CH_2)N$	+	**H^+A^-**	=	**$(CH_3)_2(CH_2CH_2)N:H^+A^-$**
TEA	+	**H^+A^-**	=	**$TEAH^+A^-$**
Amine	+	**Organic acid**		
$(CH_3CH_2)_2N:$	+	**H^+A^-**	=	**$(CH_3CH_2)_3N:H^+A^-$**

Figure 5: Chemical Reactions

Ammonium salts formed with essential oils are non-crystalline solids, have a low melting point, are yellow in color, are thermally unstable, are subject to air oxidation, and can undergo rearrangement to form more stable organic amines. The salts are formed by the reaction of the base with the acidic portion of the buffers, e.g. ammonium eugenolate, or ammonium acetate.

Ammonia has been found to be virtually 100% removed within 15 minutes after treatment with the oil mixture both in a laboratory and in actual situations. The oil mixture is more efficient in removing stronger bases such as TEA and DMEA, which may be present as malodors. Their concentration levels may be reduced to less than 0.1 ppm on contact. The essential oil mixture was titrated versus a standard solution of ammonia. It was found that 1 mL of the oil mixture was needed to neutralize 0.00012 g. of NH3. Because of the solubility and distribution factors mentioned previously, the total amount of NH3 removed from the environment would be much larger than the amount predicted from chemical reactions alone. The number of g. of NH3 removed by 1 mL of the oils may be as high as 0.012 g.

In the case of NH3 we are dealing with a substance that is very soluble in water, and is very reactive at lower pH values. We therefore would expect the difference between the bulk prediction and recalculated values, which would correct for gas-phase diffusion neutralization due to NH3 uptake, to be more pronounced. The increase in gas uptake would be a much larger factor, possibly as much as 20 or 100 times as great. In an attempt to visually see this effect a theoretical chart of expected values for NH3 was constructed and is shown in Figure 6.

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[3] Ecosorb was tested for toxicity in accordance with EPA Regulations and was found to have no positive eye irritation reactions, had a zero dermal irritation score, (Toxicity Category IV for skin effects), not to be toxic by 6 oral ingestion at the 5 g/kg level (Toxicity Category IV), not toxic by dermal application (Toxicity IV), had no positive Buehler tests for skin sensitization, tested, not detected, for halogenated hydrocarbons and tested, not detected, for harmful volatile organics (protocol 624). [4] Results available on request.

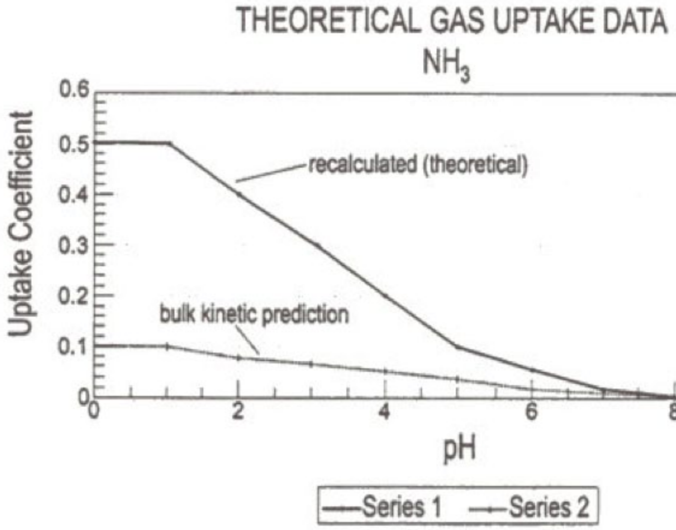

Figure 6: Theoretical Gas Uptake

It would seem that the efficiency of essential oils in holding onto gaseous substances such as SO_2, H_2S, and NH_3 is a function of the misting efficiency (size and speed of the droplet), the solubility of the substance in water (which is facilitated by the organic nature of the essential oils a variable not studied in the above mentioned paper), and the chemical reactions (chemisorption) taking place between active ingredients in the oils and the gas.

Summary: Selected essential oils will effectively remove the basic malodors NH_3, TEA and DMEA by a combination of mechanisms including an acid-base reaction, increased solubility due to pH factors, and changes in distribution constants. A portion of the amine forms a non-crystalline solid ammonium salt, which is readily removed from the air during the scrubbing process. The remaining amine dissolves in the essential oil/water droplet and is strongly held in the droplet due to changes in its solubility and distribution constant. Amines have been shown to be virtually removed within fifteen minutes after contact with the mixture.

Mechanisms for Acidic Malodors:

Acidic malodors include hydrogen sulfide, sulfur dioxide, chlorine, alkyl mercaptans, phenols and other volatile acids. An essential oil mixture will have the same general mechanism for attracting these acids as it does for ammonia. In this case the pH of the mixture should be adjusted to 6.0 - 6.2. The higher the pH will more greatly affect the absorption of hydrogen sulfide, and other acidic gases. The gases will chemically react with the oil buffers forming organic salts, and by adding across double bonds in conjugated components of the oils, forming new, derivitized essential oils. The chemical reactions and pH adjustment will greatly increase the efficiency of removing acidic gases from the atmosphere. The pH of the essential oil mixture is typically at a pH of 6.0 when used.

Sulfur dioxide is an oxidant gas and exposure to it alters pulmonary immunologic responses and increases the host's susceptibility to bacterial infection. The gas reacts readily with water and forms sulfurous acid, which is an irritant.

The above-mentioned compounds are acids, or will form acids when in contact with water. The compound H_2S has been tested and believed to react with Ecosorb by addition across a double bond as well as by a neutralization mechanism. Several compounds in the mixture contain double bonds, which can react with acidic malodors.[1] Compounds containing a conjugated system of double bonds, one of them being an electron-withdrawing group such as a carbonyl (C=O), which facilitates the addition, will more readily react with these acids. A solution of H_2S underwent a pH change from approximately 4.0 to 6.0 when it came in contact with the oils, indicating the elimination of this acid. Infrared studies of the reaction of H_2S with a conjugated aldehyde show loss of one of the aldehyde's double bonds. Experimental data indicates the H_2S is removed by the reaction shown in the following reaction. When the double bonds were removed through the addition of Br_2, the oils proved to be less effective in removing these malodors.

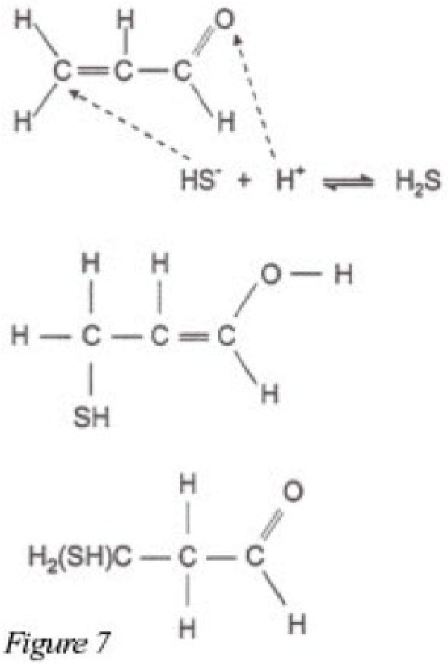

Figure 7

Hydrogen sulfide, when in an aqueous media, can also be air oxidized to form free sulfur. This may also happen to organic sulfides. Mercaptans react using the mechanism illustrated above. Ionization of these compounds is shown below. Malodors, such as hydrogen sulfide, that have not reacted chemically, but have dissolved in water droplets, will oxidize over a period of time. The oxidation products will be less volatile and therefore will no longer produce an odor problem.

$CH_3CH_2SH \quad \sim \quad CH_3CH_2S^- + H^+$

$CH_3SH \sim \quad CH_3S^- H^+$

$SO_2 + H_2O \quad \sim \quad H_2SO_3$

$H_2SO_3 \quad \sim \quad H^+ HSO_3^-$

Figure 8: Ionization

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[1] Yet unpublished research by Wilkinson and Zhang.

Molecular models were constructed for Phenol, HS, HSO, CHSH, and CHSH. These models were added on to a double bond in a model of a conjugated aldehyde. No steric hindrance was noted in the case of Phenol, HS, HSO, and CHSH, and only slight hindrance in the case of CHSH. Models of higher molecular weight mercaptans showed considerable steric hindrance indicating difficulty in reacting by the suggested mechanism.

Acidic malodors will also react with the aforementioned buffers forming organic salts. It was found that 1 mL of Ecosorb reacted with 0.000118 g. of SO_2, and as in the case of NH_3 this value could be as high as 0.0118 g. There are three major factors effecting the removal of an acidic gaseous malodor from the environment: (a) uptake as a function of pH, (b) modeling of the gas uptake (Henry's Law), and (c) interaction at the interface. The following chart was used to discuss the uptake of the gas SO_2 by fast moving water droplets.

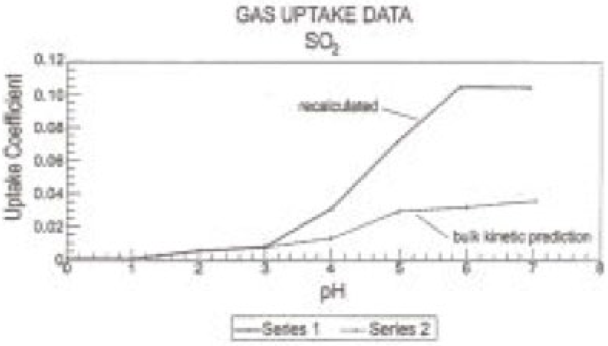

Figure 9: SO_2 Uptake Data

The lower curve represents the bulk kinetics prediction, or the amount of SO_2 we anticipate being removed by liquid water. The Y-axis (uptake coefficient) relates to the relative amount of the gas being removed. Under normal conditions we would anticipate SO_2 dissolving into the droplets of water more efficiently at a pH of 4.0 to 7.0, since the gas is an acid anhydride and will react chemically much better as the pH increases. This lower curve considers primarily the solubility of SO_2 at the pH listed. The upper curve is what we actually find when studying removal of the gas under fast-moving droplet conditions. We observe a 4 fold increase in removal efficiency caused by a combination of the above listed factors:

a) SO_2 is more soluble in water that is less acidic, reaching a maximum at a pH of 5.0. The fact that the droplets are small and fast moving causes more collisions, and increased surface resulting in a more efficient removal of the gas when using a mist.

b) Because of the limited solubility of SO_2 in water, re-evaporation of the gas due to Henry's Law is important. A portion of the gas would be lost due to this equilibrium. However, it is believed that $SO_2(g)$ enters the liquid droplet not as $SO_2(aq)$, but via a surface complex. Under these conditions, since there is increased surface area, surface complex formation would be increased in the presence of a second chemical substance. This leads to:

c) Interactions at the interface. This constitutes a chemisorption process in which, in the present case, $SO_2(g)$ collides with a water molecule at the interface and forms a complex such as HSO_3^-. The effect of fast moving, extremely small droplets combined with the above mentioned three factors make the removal of SO_2 more efficient when the sample is misted with small droplets of water than when we look at reactions of water solutions (H_2SO_3) of the gas. In the article we find that the recalculated gas uptake values are greater than the bulk kinetic prediction by a factor of 4.

Wilkinson and Zhang determined hydrogen sulfide levels in a field test using an MDA Zellweger monitoring device. This instrument produced higher readings at high humidity versus low humidity using identical concentrations of hydrogen sulfide. Hydrogen sulfide levels apparently remained constant when sprayed with a water solution of essential oils when measured with the MDA device. However, when a filter containing silica gel was attached to the instrument's intake line hydrogen sulfide levels decreases from 15.7 ppm to approximately 1 ppm in twelve minutes. It is apparent that if one is interested in determining hydrogen sulfide gas alone and not in hydrogen sulfide dissolved in water, then a water-removing filter must be added to the system. For proper analysis of hydrogen sulfide gas in a gaseous sample an instrument must be used that: (a) does not use heat to vaporize the sample, (b) is specific for the gas only, and/or (c) contains a hydrophobic filter to prevent hydrogen sulfide dissolved in water from being analyzed as hydrogen sulfide gas.

Summary:

Selected essential oils have been shown to be effective in removing the malodors Phenols, H_2S, SO_2, C_2H_5SH, and CH_3SH from a contaminated atmosphere. Sulfur dioxide, methyl mercaptan, and ethyl mercaptan were reduced to less than 0.1 ppm on contact with Ecosorb. Hydrogen sulfide took as long as 15 minutes for removal. Selected phenols were also effectively removed. Acidic compounds capable of ionizing in water, and not having bulky anions which would cause steric hindrance, will react with specific compounds contained in the product. Compounds listed in this section meet these criteria. Acidic malodors will also react with the natural buffers to produce organic salts.

Mechanisms for Neutral Malodors:

Neutral compounds such as benzene and styrene are less soluble in water than acids and bases. They are also less chemically reactive with most essential oils. At the present time little research has been done on these compounds. It would seem that pH would have less of an effect on solubility and on the distribution constant. The electrostatic oil film around droplets would still act to facilitate the removal of these gases, but the overall effectiveness in removing the gases would be much less than with the aforementioned compounds. Styrene can react with itself under basic conditions to form polystyrene. There are compounds in the essential oil mixture that have a conjugated system similar to styrene. It is proposed that the mixture's pH be adjusted to levels of 8.0, 9.0, 10.0 to study the effect of these higher pH's on the removal of styrene. Additional modification of the scrubber and the oils will be made to increase the efficiency of removing styrene from the environment.

CONCLUSIONS

The most universal scrubber for malodors is water. However, water offers some disadvantages including its rapid loss of dissolved gases. The uptake of a gas into water is a function of (a) pH, (b) gas phase diffusion, (c) re-evaporation due to Henry's Law, (d) change in polarity of water due to polarity modifiers and (e) interactions at the interface. Ecosorb facilitates the removal of malodors by chemically reacting with the gas itself, by changing the pH and affecting the solubility of the gas in water, by increasing the organic makeup of droplets of water, and by possibly increasing the distribution constant between the gas and water. The effectiveness of Ecosorb in removing high concentrations of malodors is measured more by its influence in solubility and the distribution constant of malodors in water than in its specific chemical reactions. The effectiveness of the product in removing low concentrations of malodors is related primarily to the chemical reactions involved, and less to pH and atomizing characteristics.