Malodor: the neglected opportunity

By James P. Cox, PhD

To say that the least understood and most troublesome problem encountered in air pollution work today is malodor falls just shy of understatement. As the technology to deal with this problem is collected and understood, it will become apparent that the conditions described in the foregoing statement are not, as a matter of fact, justified.

It is true that the underlying phenomenon of olfaction, its physics, biophysics, and psychology are not yet well defined. This undoubtedly has many adverse affects in practical odor control work. It does not mean, however, that a practical technology does not exist, for it almost certainly does. The constraints that exist in this troubled area result largely from lack of true knowledge at all levels by those engaged in it. For example, there is a belief virtually universal among pollution authorities and industry that chemical additions, especially if they are perfume materials, to malodorous effluents simply will not work. That all odors are chemical and will respond to chemical alteration goes unnoticed in this belief.

The result is that all sorts of hardware and equipment are required by authorities and installed by business in an attempt to solve the problem. With very few exceptions, it should be evident that the only time any equipment works at all is when it incorporates chemicals of some form. It should be overwhelmingly clear that chemicals and only chemicals can solve odor problems. That it is not clear is robustly evident in the present confused state of the art.

Those engaged in the manufacturing process and sale of essential oils, esters, and other odor-affecting materials have permitted the belief that their materials are of little value in malodor control to develop. This is peculiar considering that over fifty percent of all complaints registered nationally by pollution authorities concern malodor. It is more peculiar yet when even the most cursory examination of this troubled area reveals the failure of the technology which is being applied to solve the problem. Many industries are in dire trouble because of malodor and would welcome relief.

By and large, the practice of enforcement officers and engineers is to deprecate to a degree of absurdity the actual value of perfume (chemical) solutions. If this were done in light of reasonable working alternatives, it might be understandable. In most cases the alternatives are not reasonable economically, and in addition, they normally do not solve the problem. As a matter of fact, it is not uncommon to see statutes which specifically eliminate perfume solutions under such terms as "masking." Masking actually has little, if any, scientific meaning. Strange, indeed, that the fragrance industry would allow this opportunity to become abandoned by default.

The most desirable solution when dealing with malodor as a public nuisance is one which results in elimination of the malodor problem. This is seldom possible to accomplish entirely. However, there are reasonable alternatives such as the reduction and/or alteration of the unpleasant to pleasant.

The basis of industry's compliance to pollution control standards in most jurisdictions takes many forms and guises but, as a matter of fact, is based on only one reality—complaints. Any solution which will result in successful reduction or elimination of complaints should not be denied, but unfortunately in many cases the very people who are the most accomplished in addressing the malodor problem are forbidden by statute from even trying. Why? Malodor, where it is not toxic, is a matter of ugliness. The fragrance industry's business is to alter the state of ugliness, and malodor problems fall well within the parametefs of its expertise and is part of its legitimate domain. When perfume solutions to this problem are discussed, no excuses should be made for the use of masking agents for, as already stated, masking is an imprecise term. Many real changes can and do occur upon addition to malodorants of perfume preparations. Masking is only one of numerous possibilities and is not a particularly desirable one, in most cases. If the malodorant to be treated is studied in its component form, many things can be done to alter the components until the problem is eliminated, reduced, made pleasant, or altered favorably.

Activated carbon, where practical to use, is an efficient tool of odor control technology. It should be remembered, however, that adsorption is a Van der Waal's (chemical) phenomenon. It should also be remembered that water used extensively in odor abatement equipment is a chemical in the truest sense of the word.

Some malodors encountered are simple but most

are far more complex than widely believed. When odors are simple, the solutions may be chemically simple; when they are complex, the solutions are complex. Complex odor alterations are based upon their chemical behavior. The solutions, then, lie not in additional or more elaborate equipment, but in better and more efficacious chemical solutions, and practical applicators, hopefully, with a concomitant lessening in use of precious water and fuels. If solutions are to be found, they will come almost entirely as a result of chemical alterations. Some old thinking will need to be revised.

For example, among the arsenal of treatments which soon, hopefully, will be properly used to eliminate odor problems is application of essential oils, aroma chemicals, and other odorous materials, often referred to as perfumes, deodorants, and reodorants. Present feeling among pollution concerned circles is instant rejection of such a solution.

This must be a result of some atavistic emotion toward the nostrum and snake oil salesmen who once plied the trade. Actually, there is a valid and potentially wide application of this type of remedy and like other steps required to reduce or eliminate a complex odor problem, it is but one component, albeit perhaps the most important component.

Bad odor is very difficult to define since it is a highly subjective reaction phenomenon. Where it does exist, it is probably a cosmetic problem. Presently required solutions of industry, if applied to individuals suffering from metabolic disorders and producing strong, perhaps unpleasant body odors, would require the wearing of suits of armor, some with internal showers, some with cyclone effects, some with torches burning at vent sites, or alternatively and probably in spite of such measures, being driven from society altogether. This would be strange treatment indeed. Furthermore, the persons to be treated this way may be performing vital services. Could they continue under such impositions? Probably not. Neither can industry. Unfortunately, the smell of success is not always sweet.

The success of any odor control measure depends on proper analysis of the malodor composite; proper formulation to eliminate, reduce, or cosmetize it; and proper application. For example, if the malodorous gas is highly alkaline, the simple expedient of a shift in pH may result in considerable odor reduction.[1] Many processes of biological material evolve considerable quantities of ammonia and ammoniacal effluents. The simple expedient of addition to a malodorous system of citric acid,[1] glacial acetic acid[1] or other acids in minute amounts can at once resolve this problem. The residues can be collected in scrubbers or released in the form of resulting low or non-odor bearing acetates.

Further, a major component may represent a base for esterification.[1a] In itself a malodorant such as amyl, isoamyl alcohols, butyl alcohol, or mixtures when treated with appropriate acids via the fogger will result in the esterification *in situ* of the alcohols to very pleasant odors. Why not? The issue is one of *mal*odors, isn't it? Of course, this is frequently overlooked in odor control work, but where reduction is insufficient to eliminate or reduce the degree of unpleasantness, why not?

To replace the unpleasant with the pleasant is a widely acceptable and long standing social alternative to elimination. If it were not, there would be no deodorants sold, for no one would buy them and no one would use them. Ugliness is an essential aspect of many processes including rendering, meat packing, garbage disposal and countless others. It cannot be eliminated.

In most cases, malodor components can be altered, suppressed, neutralized, pH'd, adsorbed, oxidized, reduced, Zwaardemakered, or catalyzed away. Any residues, if unpleasant, can be dressed up and made pleasant.

If the fragrance industry is to retrieve this lost opportunity, it must offer applicators which are functional and formulas which have been customized to the problem, and it must assert its right to serve this lucrative and growing area of public concern. To the corporations who are willing to seize this opportunity will come great satisfaction of valuable public service and concomitant reward.

Various perfume techniques can be employed in formulation of a specific solution to treat a malodor problem (see table). In addition to these methods of odor control all of which may be readily applied via a vaporizer, aerosol generator, or in scrubbing solution, is the practical control of vectored odors.[18] Overlooked in modern odor control technology is the phenomenon of material and color adsorbency affinities for odors of all sorts.[1,5,10] It is this obscurely known factor which results in odor complaints under seemingly impossible conditions, i.e. the suspect plant is inoperative at the time.

The immediate plant environment under proper conditions collects in substantial amounts odor bearing molecules. When the conditions are appropriate to overcome the adsorption phenomenon, the odor molecules are set free, often resulting in complaints. There are several ways to control this phenomenon which is really a large odor sink. The immediate area may be painted in colors with little or no affinity for the odor characteristic to it. The optimum color will vary depending on the nature of the odor.[5,10,15,18] An alternative method is to release minimal amounts of inodorous material which compete more vigorously for the adsorption sites. Many alcohols, essential oils, or esters in small amounts will compete,[18] although this depends greatly on the nature of the malodor.[5,10,15,18] For example, pyridine adsorbs on aluminum, glass, gold, lead, nickel, and silver very weakly, and transitionally resides no longer than a few seconds. It adheres more strongly to copper, zinc, and porcelain, residing for a few minutes. It adheres very strongly to iron and steel, residing for hours or, under ideal conditions, for days. Skatole, a repulsive and commonly encountered malodorant, shows no affinity for porcelain, moderate to strong affinity for glass where it will adhere for hours, and very strong affinity for metals where it will adhere for one to twenty days, or longer. The affinity of odors for the vector surface is a

pH:

Formula buffered for optimum odor null or free addition of acid or base counterpart
Reference: 3, 4

NH_3 + CH_3COOH → CH_3COONH_2
Ammonia+Hydrochloric acid→Ammonium chloride
Odorous+ Odorous → Inodorous

NH_3 + CH_3COOH → CH_3COONH_4
Ammonia+Acetic acid→Ammonium acetate
Odorous+ Odorous → Inodorous

Reodorization:

Formula containing balance of essential chemicals to esterify in situ malodor component
Reference: 1a

Mixed alcohols+Mixed acids→Esters

Zwaardemaker pairs:

Certain odors, when combined, result in reduction or elimination of both
Reference: 5

Benzoin +Rubber →ø
Bitter almond +Musk →ø
Ethyl mercaptan+Eucalyptol →ø
Oil of juniper +Butyric acid→ø
Skatole +Cedarwood →ø

Catalysis:

Some components may be readily catalyzed to inodorous or pleasantly odorous end products
Reference: 4, 5, 6, 7, 8, 9

CH_3CHO + I_2 →
Acetaldehyde+Iodine→

CH_3I + HI + CO
Methyl Iodide+Hydrogen Iodide+Carbon Monoxide

CH_3I + HI →
Methyl Iodide+Hydrogen Iodide→

CH_4 + I_2
Methane+Iodine

Adsorption:

Odors may be adsorbed on oil droplets, carbon particles or other chemicals and are either then sufficiently reduced in odor or may then be more readily collected as particulates
Reference: 1, 3, 4, 5, 10

Silica gel, oils, activated carbon, various resins, etc.

Metal ion suppression:

Many odors are reduced considerably, especially used in conjunction with an oil adsorbant or eliminated entirely by treating with metal ions
Reference: 1a, 11, 15, 16

Iron, zinc, copper, zinc ricinoleate, etc.

Oxidation:

Many malodor components may be oxidized
Reference: 12, 13, 14

$2KMnO_4$ + $3SO_2$ +
Potassium permanganate+Sulfur dioxide+

$4KOH$ → $2KMnO_2$ +
Potassium hydroxide→Potassium dioxide+

$3K_2SO_4$ + $2H_2O$
Potassium sulfate+Water

Essential alteration and Cosmetizing:

When oils and sometimes esters are added to a foul odor, the odor is eliminated after it is exhausted or in some cases results in a pleasant odor of combinations
Reference: 1, 3, 5, 10, 15, 17

Rule #112 (Moncrieff): "Many odors may be eliminated by the presence of other odors to the end that no odor at all is present or detectable."

determinant of unknown (but probably Van der Waal's) forces. Volatiles display a definite order of affinity. One will drive out another displaying a weaker affinity or be driven out by one displaying a stronger affinity. For example, eugenol or xylene will drive out allyl alcohol from paraffin, but not the reverse. Chemical scavenging by release of vector competitors in areas of processing is admirably suited to the solution of this problem.

It is obvious that the solutions to modern odor control problems will in the future be developed in light of a more thorough understanding of the chemical nature of odors and that the accent on development of control technology will rest firmly on this foundation. The development of practical solutions will result not from the hardware engineer but as a result of the odor chemist developing ingenious solutions which will be supported by hardware designs fashioned to make the best use of this new technology.

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