Malodor Control—A Review

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Through the centuries, societies and cultures have tried to eliminate bad odors from their environment. From the burning of odorant woods and herbs through incense, fragrant oils and pomades to our modern aerosol technology, the search for a more pleasant surrounding goes on.

Malodor

It seems that most malodors relate to certain smells that, at some time in human evolution, had signaled imminent danger: such are the odors of smoke, carnivorous animals, decaying flesh, spoiled food and even the smell of our own species.

In modern times, these objectionable odors come from many and diverse sources. Just to mention a few, let's cite industries of all sorts, rendering plants, garbage dumps and, even closer to home, household and body odors as well as for us perfumers the off-odors of many product bases.

We can classify most of the chemical substances perceived as malodors in six major groups

—Lower aliphatic carboxylic acids present in most rancid, sweaty and bathroom smells

—Lower aliphatic amines perceived as fishy, urinous and sweaty

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—Lower aliphatic mercaptans and thio acids, such as butyl mercaptan and thio glycolic acid, part of bathrooms, cooking (cabbage) and depilatory and cold wave odors

—Thio esters, sulfides and disulfides with a rotten egg odor

—Lower substituted phenols and phenol esters such as paracresol and paracresyl isovalerate occurring mainly in bathroom odors

—Skatol with a fecal smell and present in bathroom odors

We should add to the list certain proteins used in hair treatment products the odors of which vary from meaty to burnt chicken feathers.

Olfaction and Olfactory Systems

For almost a century, scientists have been studying the mechanism of olfaction. Many hypothesis have been proposed, but only a very few are still considered by modern researchers. Four or five theories survived and have been developed by several followers. All these theories postulate that the odor stimulus is conveyed and detected at a very close range or after impact with the sensory receptors.

The Chemical and Stereochemical Theory. The stimulus is a function of the chemical reactivity. The olfaction is a chemical sense. In this theory, the stimulus is produced by the sizes and shapes of the molecules; the total perception is a combination of a fixed number of primary sensations.[1]

The Penetration and Puncturing Theory. Chemical molecules would enter the receptors and, because of their sizes and shapes, would puncture a lipid membrane separating ions thus initiating a nerve impulse.[2]

The Vibrational Theory. The impulse is modulated by the molecular vibrational frequencies of the chemical. The olfactory nerves would possess a series of receptor molecules which would vibrate in resonance to a given molecular frequency.[3]

The Functional Group Theory. The form, bulk and disposition of the functional groups of the molecules are the main factors in determining the intensity and the quality of the odor.[4]

The Enzyme and Receptor Protein Theory. Since almost all chemical transformations in living organisms are carried by enzymes, it was logical to look in their catalytic functions to explain the process of olfaction. This theory has been more recently revived and modified by Dr. A. A. Schleppnik into the "Enzyme Model of Olfaction" explanation.[5] Enzymes being of proteinaceous nature, it was a natural step to consider the possibility of the interaction of protein molecules with chemical molecules to initiate the nervous stimulus.

Some experimental evidence for the involvement of receptor proteins is available now. Studies of animal receptor sites in the nasal mucosa have shown that specific proteins were binding to certain chemical structures.[6,7] It seems that this is the prevalent theory now. Several specific proteins occupy a non-specific receptor site such as olfactory cilia or olfactory rods.

The olfaction process is probably complicated by the presence of enzymes which change certain odorant's molecules in situ.[8]

We can recognize four steps in the olfactory process. The first is the stimulus or signal generation in which the receptor protein or site reacts to the odorant and generates a nervous impulse. Second comes the transmission of the signal although very little is known about the modality of transmission to the brain through the olfactory nerve.

In the third step, perception, the olfactory brain translates the nervous stimulus into an odor. Through a final complicated process, cognition, the brain looks for familiarity of odor which is in turn translated into a known odor category and we will say, "It smells like a rose." This step is very important in human evaluation of odors and it is that step which makes us separate good from bad smells. This recognition of odors varies somewhat from culture to culture and with the background of the individual. The process is even more complicated when a blend of odorants is evaluated.

Perception of Odorant Mixtures

First, we should point out that the human nose is not extremely sensitive to odor intensity variations. The range of perceptible changes varies from 20-30% of the initial intensity. By contrast, the human nose is very sensitive to variations in odor quality.

The most difficult judgment to make with reliability is to evaluate the intensity of a mixture of odorants, since the odor quality interference has to be kept at a minimum. The more complex the mixture is, the more the intensity judgment is subject to errors due to the change in odor quality.

If we limit ourselves to binary or tertiary mixtures of odorants in close range or intensity, the odorivector addition (Berglund) is applicable (see figure 1). This approach cannot predict positive synergies where the mixture odor is more intense than the sum of the components. Very few positive synergies have been studied but all perfumers could mention a few they have encountered in their professional lives.

This review of the different theories of olfaction and of the odorant mixtures perception brings us to the interesting subject of malodor control.

Malodor Control

The first approach to malodor control is to stop the formation or the release of the objectionable odor. This is done through the use of disinfectants and bacteriostatic agents (personal deodorants).

The aspect which interests us primarily here is the use of another odorant or mixture of odorants against malodors. The different approaches taken for that purpose relate to three aspects of the same effect, that is the resultant total intensity of a mixture is almost always inferior to the sum of the components' intensity.

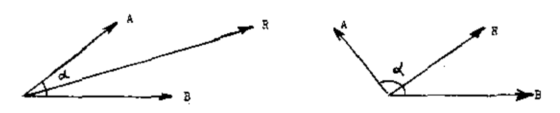

Figure 1. Odorivector Theory. (Berglund 1973): In a binary mixture, the total odor intensity is inferior or equal and very seldom superior to the sum of the components' intensity. In tertiary and more complex mixtures, the vector summation theory predicts a higher overall intensity than really perceived.

$R^2 = A^2 + B^2\ 2AB\ Cos.\ \alpha$
If angle $\alpha = 0$ (direct addition)
If angle $\alpha = 180°$ (if possible, direct subtraction)

Incorporating an objectionable odor in a fragrance blend is the technique which is generally used when a base odor has to be corrected without using a high intensity fragrance. It is also applied, besides the bacteriostatic effect of certain aromatics, to the "Deo-Cologne" approach where the residual sweaty odor is "built-in" to an acceptable fragrance.

Another approach is masking an objectionable odor with a fragrance of high intensity so as to interfere with the perception of the malodor and make it less obvious.

The third technique involves counteracting an objectionable odor with a fragrance of fairly low intensity, this fragrance being specially formulated to "counteract" the malodor perception.

In all three cases, we can apply the odorivector theory. When the angle between the two component's vectors increases, the resultant decreases. By carefully selecting the fragrance blend, it is feasible to decrease the perception of an objectionable smell.

When the decrease of malodor intensity is minimal, a strong fragrance is necessary to make the overall odor acceptable and we have a "masking effect." When the decrease of malodor intensity is important, a very low level of fragrance is required and we have a "counteracting effect." We have experimented with many different odorants and we have selected two aromatic chemicals to demonstrate our point.

Experimental Conditions

The malodor used is shown in Formula 1. All tests were conducted in a bathroom 8 feet by 8 feet with tiled floor and walls.

All the evaluations were performed by a panel of six evaluators. The odor intensity scale was from zero to 100, 20 being threshold of malodor perception, 60 being moderate intensity and 100 being high intensity. The concentration factor in the room is a function of two constants: concen-

Table I. Determination of Malodor Concentration

Time sprayed	3.00 sec.	9.00 sec.	12.00 sec.	21.00 sec.	30.00 sec.
Concentration factors	.05	.15	.20	.35	.50
Log (CF x 10^2)	.698	1.176	1.31	1.544	1.69
Rounded to (a)	.70	1.20	1.30	1.50	1.70
Intensity (averaged) (b)	35.00	65.00	75.00	85.00	100.00

Spraying time of 21 seconds will be used as the malodor target for all subsequent tests.

(a) X axis in Figure 2
(b) Y axis in Figure 2

tration (C) in aerosol can and spray rate (SR) in gram/sec. and one variable: spraying time (ST) in seconds. The definition of the concentration factor is CF (Concentration Factor) = SR x C x ST.

The malodor concentration was determined to arrive at a realistic level of malodor to be used as the target of subsequent evaluations (see Table I and figure 2). The fragrant material concentration was determined following the same steps as for malodor determination. Two aromatic chemicals, cyclohexyl ethyl acetate and benzyl propionate, were selected because of their close overall intensity and related odor quality: a concentration of .1% in aerosol can and a spraying time of 3 seconds rated at an overall odor intensity of 45/50. The concentration of the fragrant part was subsequently increased by increasing spraying time.

Results

As can be seen in Table II and figure 3, the addition of cyclohexyl ethyl acetate to malodor results in a noticeable depression in the overall intensity to reach a plateau, then an increase. This can be expected and follows somewhat the vector addition rule.

But, if we consider the perceived malodor aspect, we see the intensity drops quite drastically below threshold which means that a small amount of odorant (fragrance) would be necessary to alleviate the slight dirty residue of malodor. This aspect of the graph is typical of the so-called "malodor counteractancy" principle.

In another aspect of odor addition with benzyl propionate, we see the expected decrease but also a more rapid increase in overall intensity (see Table III and figure 4). The most striking difference is in the intensity of the perceived malodor component. The perception of malodor decreases very slowly and through extrapolation we can see that it would take a concentration factor of 10 equivalent to a spraying time of about 1 min. 40 sec. with an overall intensity increased well over the original malodor intensity. This area is where masking occurs.

Formula 1

Malodor used in tests	%
Isovaleric acid	0.90
Isobutyl mercaptan	0.90
Scatol	0.90
Thio naphthol beta	0.90
P.cresyl isovalerate	2.00
N.methyl morpholin	6.00
Caproic acid	6.00
Thioglycolic acid	20.40
Dipropylene glycol	62.00
	100.00
Aerosol can be filled with	
Malodor	0.01
Dipropylene glycol	4.99
Hydrocarbon propellant	95.00
	100.00

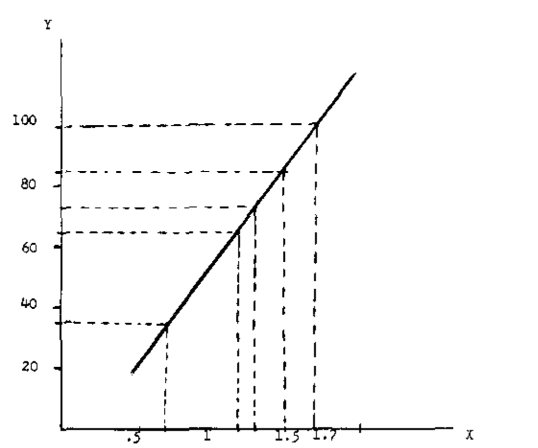

Figure 2 (see also Table I)

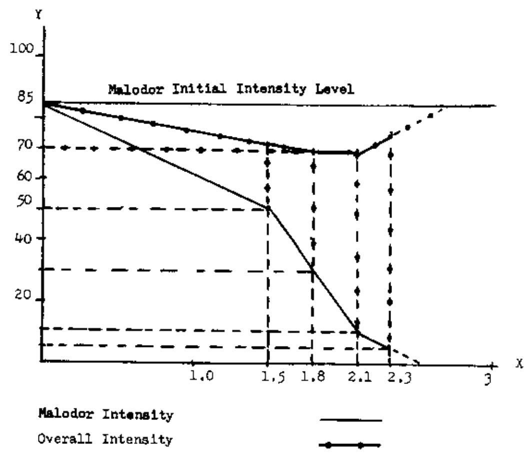

Figure 3 (see also Table II)

This experimentation has been performed on a certain number of fragrance chemicals. These aromatics presented the same types of behavior and could be classified either as maskant or counteractant.

Practical Applications

Malodor control in consumer products has been the subject of many different studies. Different approaches have been used.

Applying the principle that "what does not get to the nose does not smell," certain techniques tried to suppress the volatility of undesirable odors. But what gets to the nose smells, and this is true for bad as well as desirable odors. That is why the delivery rate of the fragrance as well as its volatility is of the utmost importance, so that it reaches the nose with the malodor.

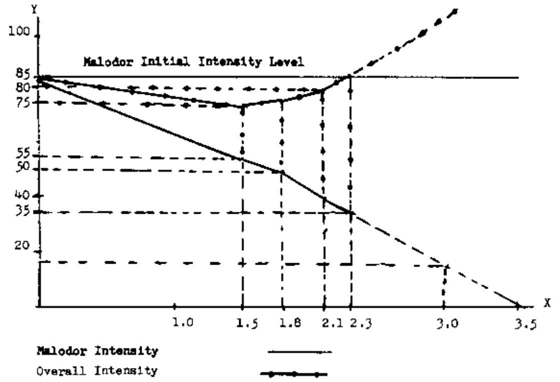

Figure 4 (see also Table III)

Table II. Malodor Counteraction Evaluation of Cyclohexyl Ethyl Acetate

Concentration of cyclohexyl ethyl acetate in spray can: .1%
Spraying time of malodor: 21 seconds for an intensity of 85
Panelists evaluated overall intensity/malodor intensity

Spraying time of odorant	3.00 sec.	6.00 sec.	12.00 sec.	18.00 sec.
Concentration factors	.30	.60	1.20	1.80
Log (CF x 10^2)	1.47	1.78	2.08	2.26
Rounded to (a)	1.50	1.80	2.10	2.30
Overall intensity (average)	72.00	70.00	70.00	75.00
Malodor intensity (average) (b)	50.00	30.00	10.00	5.00

(a) X axis in Figure 2
(b) Y axis in Figure 2

Table III. Malodor Masking Evaluation of Benzyl Propionate

Concentration of benzyl propionate in spray can: .1%
Spraying time of malodor: 21 seconds for an intensity of 85
Panelists evaluated overall intensity/malodor intensity

Spraying time of odorant	3.00 sec.	6.00 sec.	12.00 sec.	18.00 sec.
Concentration factors	.30	.60	1.20	1.80
Log (CF x 10^2)	1.47	1.78	2.08	2.26
Rounded to (a)	1.50	1.80	2.10	2.30
Overall intensity (average)	75.00	77.00	80.00	85.00
Malodor intensity (average) (b)	55.00	50.00	40.00	35.00

(a) X axis in Figure 2
(b) Y axis in Figure 2

Masking of malodors by applying a high level of fragrance has been used for decades. I believe that a better understanding of the so-called "odor counteraction" will be the next approach to malodor control. This technology is applicable to personal deodorants and Deo-Colognes. It can also solve many base odor problems.

But I think that the major field of application is the environmental fragrance market. We have seen many different delivery systems developed for space deodorants and reodorants. Aerosols came, were replaced by gels, then solids of all kinds claiming time-release such as entrapment, then polymers, waxes and others. All tried their luck on the market.

The best and most efficient delivery system is still the aerosol can and this approach has come back very strong. We see the purely malodor-solving products evolving into more appealing "space perfumes."

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