Adhesives and Odour

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Abstract
Odour, or rather the absence thereof, is gaining an increasing importance as selection criterion for adhesives. Typical examples in which this topic plays in important role include the hygiene, the building and the automotive industries. All types of adhesive are affected, regardless whether they are 100% solid systems (reactive or non-reactive), water or solvent-based.

The lecture will cover the following aspects

- The mechanism of odour detection by the human nose
- The nature of substances responsible for odour
- Formulation strategies to prevent irritating odours in adhesives
- Methods of odour detection and evaluation. Present and future (electronic nose)

The mechanism of odour detection by the human nose

The nose is one of the most important and also most underestimated human organ. Its place in the middle of the head, a strategic position, underlines also this important role. The function of the nose was quite important in the evolution of the human race. The nose was able to detect burn smell and was acting as a warning system. Also food, which was not fresh (for example fish), was easy to detect by the nose and helped therefore to improve the health of the people. In the past bad odour was very often related to diseases and other dangerous aspects of the human life. To illustrate this, the following two examples can be given:

- The word malaria does nothing else mean as “bad air”.
- The very distinguished smell of garlic was often used to drive away ghosts

But how does the human nose detect odours?
Odorants are carried by inhaled air to the Regio Olfactoria (olfactory epithelium) located in the roof of the two nasal cavities of the human nose, just below and
between the eyes.

Source: reference

This Regio Olfactory has approximately the size of 2.5 cm² and is larger than the retina of the human eye. The organ contains around 50 million primary sensor receptor cells. Interesting are the following facts about the Regio Olfactory:

- it is quite an old organ in the human evolution with only a few connections to the area in the brain where speech is generated. For this reason humans have difficulties to describe odours with words.
- there are a lot of connections to the area in the brain where emotions and motivations are produced. Therefore odours are playing an important role in perfumes, odour therapies etc.

If we look deeper into this Regio Olfactory we are able to recognise the Olfactory Epithelium which is covered by a layer of mucous. This mucous layer is about 60 my thick and contains a protein, which has the capability to bond aromas.
Below the mucous layer are the Olfactory Receptors. These receptors contain a hydrophilic and also a hydrophobic area. At these receptors the molecules are absorbed and an electrical impulse is transmitted to the brain. The Olfactory Receptors have an average lifetime of approximately 40 days.

A human is capable to recognise around 10'000 different substances. But he has some problems to describe them. An expert who designs new perfumes is able to describe 300 different expressions, which can be broken down into 74 groups. Only 27 of 74 groups are often used; like bananas, pine apples, pears.

Source: reference

Source: reference
Beside the Olfactory Receptors there is another sensory form called “Trigeminal Nerve” receptors. These receptors are widely spread in the area of mouth, eyes and nasal cavities. Substances, which are stimulating the Trigeminal Receptors, are described as hot, cold, tingling or irritating. A typical example is menthol, which in low concentrations produces a “cold feeling”. This system is less sensitive then the Olfactory Receptors but not less important. It works as a back up system and is able to recognise dangerous substances like ammonia gas even if the Olfactory Receptors are blocked.

The nature of substances responsible for odour

In the past few years a number of different theories about the relation between molecular structure and odour have been developed. The

- the steric theory of odour and
- the Vibrational Induced Electron Tunneling Spectroscope Theory

have delivered the basics for many explanations. Beside these theories about the mechanism of developing odour there are other facts that have to be considered. To produce an odour a molecule must fulfil the following characteristics:

- must have some water solubility
- sufficiently high vapour pressure
- low polarity
- some ability to dissolve in fat (lipophilicity)
- surface activity
- molecular weight must be below 294

The Steric Theory of Odour

Linus Pauling, who later received a Nobel Laureate, indicated 1946 a correlation between a specific odour and the molecular shape and size of a substance. He stated that chemicals could only be smelled if they fit into a complimentary receptor cell located in the olfactory nervous system. This so-called “Lock and Key” approach was further developed by John Amoore who proposed five primary odour and structure relations.
camphoraceous: football shaped molecules

musky: necklace shaped molecules

peppermint: wedged shaped molecules
Putrid and pungent smells were explained with the distribution of the electric charge in the molecules. Putrid molecules (like hydrogen sulfide) have a build-up of strong negative charge in the molecules and are attracted by the positive sites on the “putrid” receptors. Pungent molecules (like acetic acid) have electron deficient regions that are strongly attracted by “pungent” receptors, which are electron rich.

With this theory it is also explainable that a molecule can lock into more than one receptor and produce therefore also a more complex odour pattern. John Amoore explained the almond odour of benzaldehyde by showing, that the shape of the molecule could fit into camphoraceous (football shaped), floral (tadpole shaped) and peppermint (wedged shaped) receptors.
Today it is well known that the stereo-chemical theory is an oversimplification, but it’s still useful to relate odours to molecular shapes. However, there are not just seven different receptors in the human nose, there must be thousands of different ones.

**The Vibrational Induced Electron Tunneling Spectroscope-Theory**

A typical example to show the limitations of the stereochemical theory is the completely different odour behaviour of Vanillin and Iso-Vanillin.

![Vanillin and Iso-Vanillin structures](image)

While Vanillin has a very pleasant aroma, Iso-Vanillin is completely odourless.\(^{\text{vii}}\)

In 1996, Luca Turin\(^{\text{viii}}\) has developed the so-called Vibrational Induced Electron Tunneling Spectroscope-Theory. In this theory he has found a link between the chemical structure, the vibration of the chemical bonds and the movement of the electron clouds around the molecules. Especially the interaction between the electron clouds of the odour molecules and the receptor proteins was very new and could deliver the explanation why chemically completely different molecules could have similar odours. A typical example for this effect is Camphor and 1,1,2,2-Tetrachloroethane\(^{\text{v}}\).
While both the “Steric” and the “Vibrational Induced Electron Tunneling Spectroscope” theories answer many of the questions posed, as one is solved, others arise.

Formulation strategies to prevent irritating odour in adhesives

Odour is normally not what you’re looking for if you try to formulate a new adhesive. In most cases an odour free, neutral behaviour of the adhesive is expected. Especially in a time were the sick building syndrome is a big issue, any odour in the adhesive should be avoided. As we have seen before odour receptor cells have a very good link to the brain areas where emotions are produced. If the initiated emotions are connected with bad feelings, any kind of odour could be an important factor for the sick building syndrome, even if there is absolutely not scientific reason for it.

There are many other applications where adhesives with odour are not accepted. Typical examples are the automotive and the disposable hygiene industry.

There are many different possibilities for undesirable odour in an adhesive.

- the nature of the raw materials
- the process parameters during manufacturing, storing and application of the adhesive
- ageing properties of the applied adhesives
Nature of the raw materials
Due to the fact, that only low molecular weight substances (below MW 294) are able to produce an odour, we can concentrate our view to this kind of substances. Very often monomer residues like styrene, vinyl-acetate and acrylic esters are responsible. Also oligomers in C₅, C₉ and terpene resins could be a potential source. By-products in natural resins like sulphur containing molecules in tall oil rosins are well known for producing a typical smell. Also in synthetic stabilisers, thioethers are found which develop a very unpleasant odour.

In these cases only a careful selection of the raw materials will help in the odour prevention.

Process parameters during manufacturing, storing and application of the adhesive
It is quite easy to understand that also the process parameters during the manufacturing of the adhesive could have an influence on the odour producing potential. Even if the raw materials are completely odourless, high temperature or intensive contact with air during mixing could produce some oxidation- or decomposition products (lower molecular weight!). The same effect could also happen during the application of the adhesives. The right strategy in this cases is a very accurate control of the manufacturing and/or application parameters. In some cases air has to be excluded and also the use of an effective antioxidant additive is very important.

Stripping with steam or careful evacuation of the adhesive after production will help to reduce the odour level.

Depending on the chemical base, an undesirable odour could also be produced during storage of the adhesive. Especially water based adhesives are an excellent growing media for a wide range of bacteria. Very often the bacteria’s are producing H₂S which is also responsible for the bad smell of fouling eggs. In this case the use of a good preservation agent is indicated.

Ageing properties of the applied adhesives
Also after the application of the adhesive, there are still some opportunities for developing bad odour. Decomposition due to high temperature, UV-light or micro organisms are responsible. A good stabilisation of the adhesive against this different form of attack is highly recommended.

Other strategies like masking the odour are often described in the literature but very seldom successful in reality. The risk of getting a new odour problem can be considered as quite high.
Methods of odour detection and evaluation

Odour detection and classification is one of the most difficult jobs in the analytical chemistry. Up till now we have two systems, which are used for this kind of work:

- the human nose
- the "electronic nose"

The human nose

There are three basic methods used:

a) an objective method
in this case everything (temperature, humidity, concentration etc) has to be standardised. The odour produces an electrical signal in the brain, which can be detected and measured with electrodes (fixed to the head). This method is quite expensive. A simple test will cost approximately 65’000.

b) an indirect, objective method
in this test only reflex reactions as heart rate, conductivity of the skin or breath rate and depth are controlled

c) an subjective method
In this test a certain number of people try to detect the lowest concentration of an odour that they are able to recognise. This test is widely use and can be quite accurate if the number of involved people is large enough. The subjective test can also be used for the classification of a pleasant, neutral or bad odour in an adhesive.

Interesting are also the following facts about odour recognition:

- only 12% of the people are able to recognise and describe a mixture of two odours
- only 3% of the professional perfume designers are able to identify a mixture of five odours
- women are not more capable then men in odour recognition, but they can describe it better, because their brain halves work better together

The "electronic nose"

Due to the limitations of the human nose, the flavour and fragrance industry developed in the past 10 years a so called "electronic nose". This kind of instrument was designed to analyse, recognise and identify complex odours and aromas. The output is a fingerprint typical for a certain odour. The electronic nose, like the human nose, makes an analysis of the vapours emitted from a sample and performs a classification process by comparing the sample with a data
base (the memory). The electronic noses are equipped with a combination of up to six non-specific gas sensors, which when exposed to a sample produce a unique pattern. The types of sensors in use are:

- MOS (Metal Oxide sensors): The detection principle is based on the measurement of the variation of the resistance of the metal oxide
- Conducting Polymer sensors: Similar in principle to the MOS, the change in the resistance is measured as a reaction to the sample vapour
- QCM: Quartz Crystal Micro-balanced sensors are based on the change of frequency due to the absorbing of vapour of a sample on the sensor coating. As odour molecules are absorbed the crystal which vibrates at about 10 MHz, changes in frequency

It is important to know that the electronic nose needs to be trained (calibrated) very carefully before the start. Even if this technology is at the beginning and is not yet capable to replace the human, the progress in this technique over the past ten years is remarkable.

**Summary and conclusion**

Adhesives with odour are in most cases not desired. The understanding about the principles of odour developing helps to improve the properties of the adhesives. Selection of odourless or low odour raw materials, the accurate process control during manufacturing and application and the use of effective stabiliser systems will help to reduce problems in the market place. Even if the electronic nose technology advances, it will never replace the human nose. The human nose is the instrument of our customers and the consumer; it has to be considered as the “standard” sensor.
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