

Tenacity and Fixing of Aromatic Chemicals

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The quality of a perfume oil is determined by several factors. So far as its acceptance by the consumer is concerned, decisive importance attaches not only to the actual odor characteristics and stability under the particular conditions of use, but also to the odor intensity and tenacity.

Experienced perfumers have long made use in their compositions of so-called fixatives, which can, to a greater or lesser degree, increase the period for which the odor of a perfume oil or specific components of the composition remain perceptible when used.

The experiments here described should make a contribution of practical value to the elucidation of the tenacity and fixative characteristics of some components commonly used in perfume oils. It was initially attempted to determine regularities in the behavior of aromatic chemicals in relation to their tenacity as well as to detect factors through which this tenacity could be influenced. In addition, an analysis was made of the fixative properties of certain substances generally used for this purpose. On the basis of the results obtained, an attempt was also made to determine an inherent law governing the fixative action of these substances.

Tenacity of homogenous aromatic chemicals

These experiments were carried out chiefly on those classes of substance most frequently encountered in perfumery, such as hydrocarbons, alcohols, phenols, ethers, aldehydes, ketones, and esters or lactones.

To obtain precise, reproducible results, the tenacity of aromatic chemicals was determined by measurement of the weight loss. In most cases, where the weight loss progressed continuously, the gravimetric result was identical with the tenacity determined purely by odor. This comparison will be discussed in greater detail later on.

A piece of bibulous paper with a substance of about 264 g/m² was used as the support. 0.6 g of the compound to be tested was slowly dripped onto a strip of the paper 2 g in weight and 75.84 cm² in area (15.6 cm x 4.8 cm). In all cases this amount of compound was sufficient to completely saturate the paper with liquid, so that the surface area was the same in all the experiments. In the case of viscous substances, the time needed to saturate the paper uniformly was considerably longer than in the case

of aromatic chemicals of lower viscosity. The papers prepared in this way were freely suspended in a room at about 20°C with ordinary ventilation and humidity, so that evaporation could proceed uniformly on all sides.

The weighings were usually carried out after 1, 3, and 10 hours; 1, 3, and 10 days; 1 month and 3 months, using an automatic balance that could be read to an accuracy of 10 mg. In certain cases it was necessary to make weighings at times intermediate to those scheduled.

Continuous weight loss. The results obtained had to be divided into two groups, one consisting of aromatic chemicals whose weight loss was continuous and the other consisting of those whose weight loss was discontinuous. Table I lists the members of the first group, together with the tenacities of the individual aromatic chemicals.

Figures 1-3 show the change with time of the weights lost by some substances, selected from Table I. The graphs show the amount of odorant still present at the time of each weighing. The linear forms of these curves show clearly the uniform rates of weight loss, or uniform progress of evaporation.

Of interest and practical importance are comparisons of the times for which aromatic chemicals of different structure classes and molecular sizes are retained on the paper. For example, the two C₁₀ hydrocarbons, ocimene and dipentene, were retained for only ca. 1 hour, whereas the C₁₀ alcohols linalool, tetrahydrolinalool, dihydromyrcenol, geraniol, citronellol, and isopulegol, took from 4 hours to 3 days to completely evaporate from the paper strips (see Table I and Fig. 1). It was thus immediately apparent that the functional groups have a large influence on the tenacity of aromatic chemicals, just as they do on that of dyestuffs. Moreover, the tenacity is dependent not only on the kind of functional group (e.g., alcohol, aldehyde, or ester) but also on the molecular configuration adjacent to a specific functional group (e.g., primary, secondary, or tertiary alcohol). The above-mentioned tertiary alcohols, linalool, tetrahydrolinalool, and dihydromyrcenol, required 4 to 6 hours to evaporate under the experimental conditions; the secondary alcohol isopulegol took ca. 8 hours; and the primary alcohols, geraniol and citronellol, took between 2 and 3 days.

A comparison of aromatic chemicals having the same functional group and similar structural elements makes obvious the dependence of the tenacity of these compounds on the molecular weight. Whereas hexanol (*M* 102) requires only somewhat more than 2 hours to evaporate, dodecanol (*M* 186) lasts for about 2 months (see Figs. 1 and 3). Benzyl alcohol (*M* 108) clings for about 12 hours, its homologue phenyl ethanol (*M* 122) for a little over 1 day, and 5-phenylpentanol-1 (*M* 164) for about 1½ months (see Table I and Figs. 1 and 3). Similar results were obtained from the comparison of homologous ethers and homologous lactones, amongst others. The tenacity of diphenyl oxide (*M* 170) was 2 days, that of dibenzyl ether (*M* 198) ca. 1½ months (see Fig. 2). For γ -octalactone (*M* 142) and γ -undecalactone (*M* 184), the respective values were 2 days and 2 months (see Fig. 3).

Modification of the functional group has (as already mentioned) great influence on the evaporation. For example, the conversion of geraniol to

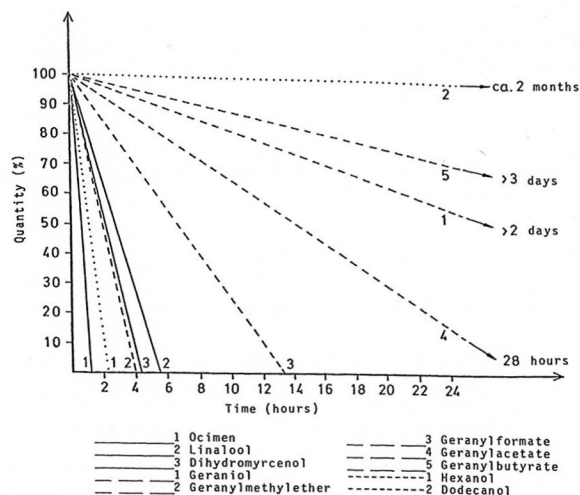


Fig. 1: Progress with time of the evaporation of aromatic chemicals (up to 24 h).

	1hr	3hr	10hr	1day	3days	10days	1mon	3mon
Ocimen	—							
Dipentene	—							
Linalool	—							
Tetrahydro-linalool	—							
Dihydromyrcenol	—							
Styrolalcohol	—							
Isopulegol	—							
Trimethylcyclohexanol	—							
Benzylalcohol	—							
Hexanol	—							
Phenylethyl-dimethylcarbinol	—							
Citronello	—							
Geraniol	—							
Dodecanol	—							
5-Phenylpentanol-1	—							
m-Kresol	—							
Eugenol	—							
Phenylethyl-isoamylether	—							
Geranyl-methylether	—							
Rosenoxide	—							
Eucalyptol	—							
Eugenol-methylether	—							
Diphenyloxide	—							
Dibenzylether	—							
Acetophenone	—							
2-Hexyl-cyclopentanone	—							
Dihydrojasmon	—							
Methyl-dihydrojasmonate	—							
Hexenylformate	—							
Benzylformate	—							
Phenylethylformate	—							
Geranylformate	—							
Decalinolformate	—							
Nonylacetate	—							
Isobornylacetate	—							
Geranylacetate	—							
Citronellolacetate	—							
Dimethylbenzylcarbinolacetate	—							
Ethylbutyrate	—							
Citronellolpropionate	—							
Geranylbutyrate	—							
Anisylacetate	—							
Eugenylacetate	—							
Phenyl-isovalerianate	—							
Isoamylcaprylate	—							
γ -Octalactone	—							
γ -Undecalactone	—							
Linalylbenzoate	—							
Benzylbenzoate	—							
Hexylsalicylate	—							
Diethylphthalate	—							
Isopropylmyristate	—							
Phenylacetaldehyde-dimethylacetal	—							
Musk Ambrette	—							

Table I: Tenacity of aromatic chemicals that evaporate at a uniform rate.

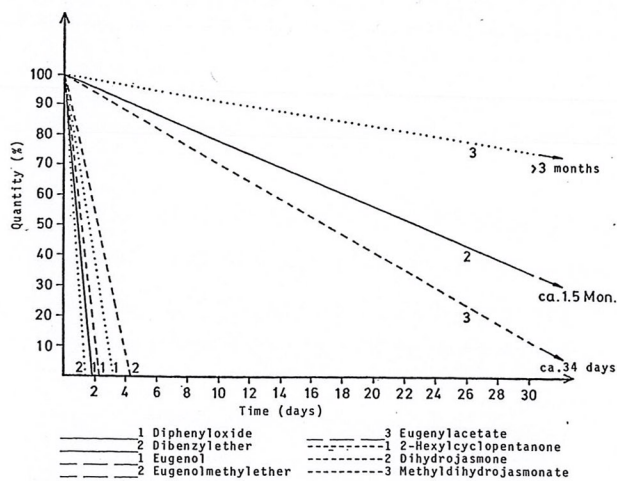


Fig. 2: Progress with time of the evaporation of aromatic chemicals (up to 30 days).

geranyl methyl ether decreases the tenacity from 2 days to 4 hours. Esterification to geranyl formate likewise brings about a reduction in the tenacity, to 13 hours. If now the size of the acid radical is increased, the tenacity increases from geranyl formate to acetate to butyrate, with times of 13 hours, 28 hours, and ca. 3 days (see Fig. 1). The series citronellol (3 days), citronellyl acetate (ca. 1 day), citronellyl propionate (ca. 3 days) displays a similar relationship (Table I) and so also do eugenol (ca. 2 days), eugenol methyl ether (ca. 4 days), and eugenyl acetate (ca. 1 month), (see Fig. 2).

There is likewise a clear parallelism of tenacity and molecular weight in the case of the formates studied. With increasing molecular size, the tenacity increases steadily from hexenyl formate (ca. 1 hour) via benzyl formate (ca. 2 hours), phenyl ethyl formate (ca. 3 hours), geranyl formate (ca. 12 hours), to decalinol formate (ca. 1 day). (See Table I.)

The introduction of an additional functional group can considerably retard the evaporation of an odorant and thus prolong its tenacity (cf. ethanol and ethylene glycol). Thus, for example, the two structurally similar compounds dihydrojasmonone and 2-hexyl-cyclopentanone require about 1½ and 3 days respectively for complete evaporation, whereas methyl dihydrojasmonate is retained for over 3 months (see Fig. 2).

All the perfumery "fixatives" that were examined showed a tenacity of at least 3 months in the experiments made. Nevertheless, the individual results were very different. Diethyl phthalate was almost totally evaporated after 3 months, but about 30% of the isopropyl myristate and musk ambrette were still present. About 60% of the linalyl benzoate had evaporated, whereas the weight of the benzyl benzoate had only decreased by 25% (see Fig. 3).

In practically all the experiments, the gravimetric and the odorous determinations of the tenacity gave identical results in the case of aromatic compounds whose evaporation progressed at a uniform rate, so that the present results provide data that can also be utilized in perfume oil compounding.

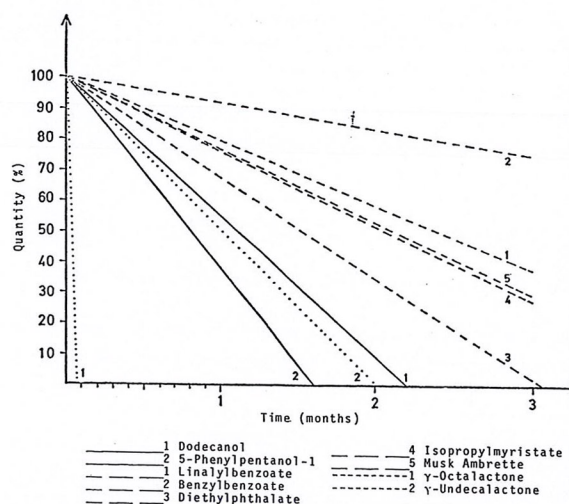


Fig. 3: Progress with time of the evaporation of aromatic chemicals (up to 3 months).

The relationship found between tenacity and structure class, functional group, and molecular weight of the aromatic chemicals shows a regular behavior of these substances and thus allows prediction of their tenacity in the rational synthesis of new odorants. The parallelism between tenacity and molecular weight can, however, be primarily attributed to connections between, on the one hand, the rate of evaporation of an aromatic chemical and, on the other, specific molecular properties, such as vapor pressure, boiling point, polarity, density, and viscosity.

One of a perfumer's skills is the ability to so use odorants with similar smell but different tenacities that a particular fragrance characteristic is emphasized throughout a prolonged period of evaporation of a perfume oil. Examples of these are the previously mentioned geraniol derivatives and the series of compounds, hexyl methyl ether, hexanol, hexyl acetate, and hexyl tiglate.

Nonuniform rate of weight loss. The behavior of those odorants that evaporate at nonuniform rates is considerably less predictable and systematic. In these cases, either a molecular alteration takes place during evaporation, or the substances tested are not homogenous but consist of mixtures of various components.

It was remarkable that none of the aldehydes tested evaporated at a uniform rate. In the course of these investigations, no odorant containing an aldehydic group was found whose evaporation rate did not diminish with increasing time.

In correspondence with this observation, heptanal and decanal, respectively, decreased in weight by ca. 70% and ca. 40% in the first 3 hours, yet had not completely evaporated after 3 months (see Figs. 4 and 6). Both substances were olfactorily perceptible for about 3 days. By means of NMR spectroscopy it was found that, under the experimental conditions, after about 2 days the residues consisted predominantly of the corresponding carboxylic acids, as was also manifested by a change in the odor. Under the particular conditions, atmospheric oxidation of the aldehydes commenced as soon as

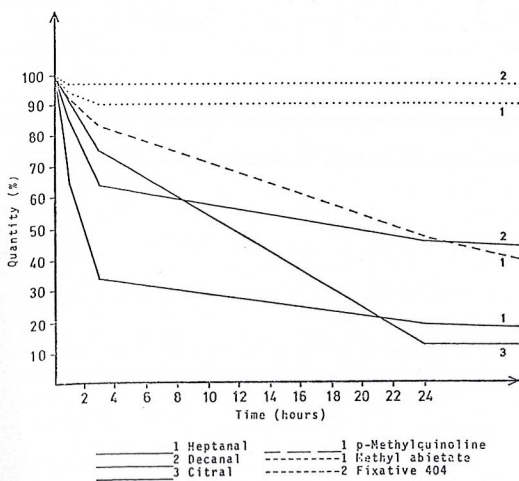


Fig. 4: Discontinuous evaporation of odorants (up to 24 hours).

the experiment started. The relatively long tenacities of up to 3 days, which were determined by olfactory assessment, can be explained as due to the considerably greater tenacities of the carboxylic acids formed. These are therefore exceptionally good fixatives for the aldehydes. In addition, because of the great intensity of the odors of heptanal and decanal, extremely small amounts of these substances can be clearly perceived.

Citral behaved in a similar fashion, although in this case almost 90% of the applied weight of material had already evaporated in the first 24 hours (see Fig. 4). The residual 10% consisted chiefly of geranic acid. In conformity with this finding, the tenacity of citral by olfactory determination was about 1 day.

Alpha-amyl cinnamaldehyde was odorously perceptible for about 10 days. After 10 days the gravimetric measurements showed that about 70% of the original weight applied was still retained by the paper (see Fig. 5). The residual small amount of α -amyl cinnamaldehyde was so greatly reduced in odor intensity by the carboxylic acid formed that it could scarcely be smelled. The α -amyl cinnamic acid formed by oxidation was retained for about 2½ months (see Fig. 6).

The two homologues, cyclamen aldehyde and p-tert-butyl- α -methyl-hydrocinnamaldehyde, revealed practically no loss in weight over a period of 3 months, so that their evaporation could be described as approximately continuous (see Figs. 5 and 6). Odorously, cyclamen aldehyde can be detected for up to 10 days, while some outstandingly sensitive noses could identify p-tert-butyl- α -methyl-hydrocinnamaldehyde even up to 3 months. In both cases, after only a few days, the amount of carboxylic acid was greater than that of aldehyde, though even after 3 months more than 30% of the original amounts of aldehyde were still present. The ready oxidizability of p-tert-butyl- α -methyl-hydrocinnamaldehyde, in particular, is well known to every experienced perfumer, since there is scarcely one bottle containing this odorant that does not have

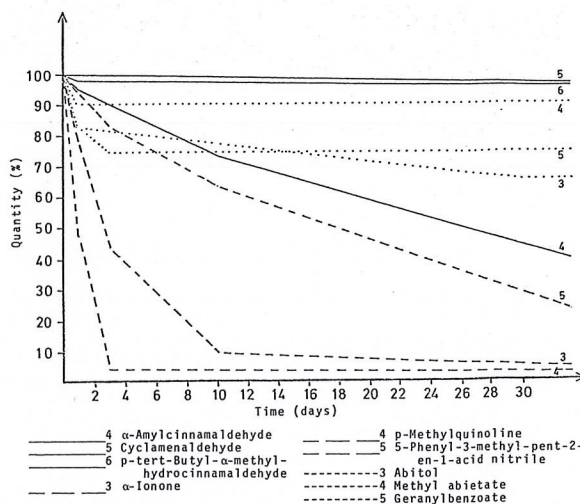


Fig. 5: Discontinuous evaporation of odorants (up to 30 days).

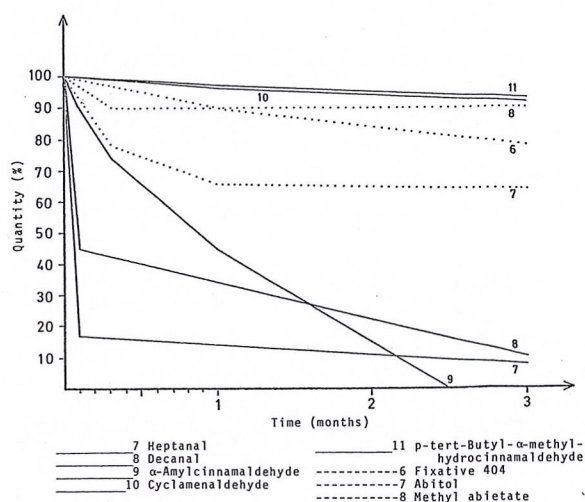


Fig. 6: Discontinuous evaporation of odorants (up to 3 months).

numerous colorless crystals around the joint of the closure, consisting simply of the corresponding carboxylic acid. Apparently the crystals of the acid occlude some aldehyde, so that even after months some traces of aldehyde are released to the surrounding atmosphere.

Even though these experimental results were precise and plausible, a systematic basis for the prediction of the tenacity of aldehydes can scarcely be discerned, since in the case of aldehydes the tenacity is dependent not only on the compound itself, but also on the rapidity of oxidation, the tenacity of the carboxylic acid formed, and the fixative ability of this acid for the aldehyde.

Nonuniform rates of evaporation were also observed, in isolated cases, among odorants that did not have an aldehydic structure. p-Methylquinoline, for example could be readily recognized by odor for 1 month, although 97% of this compound had evaporated within 3 days (see Figs. 4 and 5). The residual 3% retained a constant weight for more than 1 month, excluding the possibility of weighing error. The polymerized residues formed

in the case of this and other compounds with a pyridine structure apparently have the ability to strongly fix residues of the readily volatile odorants for a prolonged period.

Within 10 days, about 90% of α -ionone had evaporated, the violet odor also being perceptible up to that time. The residual 10% remained for over a month (see Fig. 5). Interestingly, as the time the ionone had been retained on the paper increased, a not insignificant increase in the peroxide number was detectable, suggesting that the residue left after 10 days was, at least in part, a peroxidic derivative or condensation product of ionone. This supposition was also supported by an odor reminiscent of decomposing substances.

The small, but reproducibly determinable, deviation of 5-phenyl-3-methyl-pent-2-en-1 acid nitrile from a uniform evaporation rate (see Fig. 5) can be attributed to the fact that this odorant was a mixture of the cis- and trans-isomers. The lower-boiling cis-compounds evaporated preferentially within the first day, so that the content of the higher boiling trans-isomer was progressively increased and the rate of evaporation reduced. The alteration of the cis:trans ratio as evaporation progressed could be followed by the slight change in the odor. The tenacity of 5-phenyl-3-methyl-pent-2-en-1 acid nitrile was about 1½ months, in good agreement with the value determined by olfaction.

The related compounds with extremely weak odors used as fixatives, methyl abietate and Abitol, are mixtures and in consequence their evaporation rates were far from uniform, especially in the initial phase. The methyl ester lost about 10% of its initial weight within 3 hours and then remained at constant weight over the whole 3-month period of the test (see Figs. 4-6). Abitol, in contrast, evaporated 18% of its weight in the first day, the weight loss increasing to 35% within the first month, its residual weight thereafter remaining approximately constant (Figs. 5 and 6). In agreement with these findings, the tenacity of these substances, as determined by olfaction, was more than 3 months.

The amber body well-known as "Fixateur 404"* lost weight at a uniform rate, after the first few hours (see Figs. 4 and 6). After 3 months, more than 75% of the original weight of substance was still present. According to the olfactory determination, the tenacity was about 2 months. These findings become comprehensible if it is taken into account that the odorous component, amber epoxide, is present as a solution in various almost odorless fixatives, and in addition, to round out the odor complex, there are a few percent of readily volatile odorants.

Geranyl benzoate should behave like linalyl benzoate (see Fig. 3). Remarkably, however, the geranyl benzoate lost about 25% of its weight in the first 3 days and thereafter evaporated only very slowly, so that about 70% of the initial amount was still present after 3 months (see Fig. 5). The olfactorily determined tenacity of geranyl benzoate was about 10 days. Analysis of the sample used showed that the material declared as geranyl benzoate contained about 22% of geraniol. The rapid loss in

weight during the first few days was therefore almost exclusively due to the evaporation of geraniol. The odorous assessment also related to geraniol. Pure geranyl benzoate has a tenacity far greater than 3 months and is practically odorless.

In the main, two causes for the nonuniform rate of evaporation of odorants were found: the modification of the molecule by the surrounding atmosphere and the presence of mixtures.

Atmospheric oxygen oxidized, to a greater or lesser extent, all the aldehydes studied. Oxygen was also responsible for molecular alterations in other cases, e.g., the polymerization of quinoline and peroxide formation by ionone. In practice, these oxidation reactions can to some extent be considerably retarded by an optimal addition of suitable antioxidants.

A nonuniform rate of evaporation was naturally revealed by mixtures of components with different vapor pressures. By measuring the change in weight loss with time, one can readily detect the presence of mixtures of substances, such as geometric isomers and "up-graded" odorants as well as such impurities as starting materials and residues.

Fixation of homogeneous odorants

In order to obtain specific effects in perfume compositions, it is often necessary to increase the tenacities of odorants, to a greater or lesser extent, beyond the tenacities indicated by experiments such as those described. For this purpose, perfumers have long made successful use of so-called fixatives, an investigation of whose effect on the evaporation of homogeneous aromatic chemicals will be described in some detail in the following. The experiments were carried out using different aromatic chemicals, to each of which 10% of a fixative was added. The fixatives used were: methyl abietate, Abitol, benzyl benzoate, diethyl phthalate (in part), Fixateur 404, isopropyl myristate, methyl dihydrojasmonate, and musk ambrette. In each case, the weight lost by the particular aromatic chemical was determined, without taking the weight of the fixative into consideration. If the fixative itself evaporated to a significant extent in the period of the test, the weight-loss data of the odorant were appropriately corrected.

Evaporation of fixed aromatic chemicals. On the basis of the data plotted in Figure 7, it is clear that linalool, for example, evaporated in 5 to 6 hours. The addition of 10% (reckoned on the weight of odorant) or Abitol nearly doubled the tenacity of linalool, that is, the evaporation rate was almost halved. However, it was far from possible to achieve a similar result with all the substances generally considered to be fixatives. The addition of a corresponding amount of isopropyl myristate had practically no effect on the tenacity of the odorant. From this, it was apparent that for each aromatic chemical, or each class of aromatic chemical, there was one or only a few fixatives with optimal fixing properties.

*Firmenich, Geneva.

The tenacity of citronellyl acetate was almost doubled by Abitol, whereas methyl abietate caused no increase. Citronellyl propionate was exceptionally well fixed by benzyl benzoate. In this case also, methyl abietate had the least effect of all the 8 fixatives tested, even though its use almost doubled the tenacity of the citronellyl propionate (see Fig. 7).

The rate of evaporation of an aromatic chemical was not always uniformly retarded by the addition of a fixative. In the course of these investigations it was observed that different fixatives exerted an effect on the progress of evaporation at times that greatly differed, but small deviations from the straight lines shown in the graphs were ignored in order to show the major effects more clearly.

The tenacity of the valuable "Rosenoxid" (methyl-propenyl-methyl-tetrahydropyran) was tripled by means of Fixateur 404. Isopropyl myristate caused a doubling (see Fig. 8).

The gravimetric measurement of the evaporation of fixed aldehydes yielded results that could not be reproduced in practice, i.e., as an odorous effect in

perfume oil. It could certainly be accurately determined that, e.g., heptanal was many times better fixed by Abitol than by Fixateur 404, and that the rate of evaporation of citral was approximately halved by the addition of benzyl benzoate, whereas the effect of Abitol was considerably smaller in this case (see Fig. 8), but the gravimetric results gave no indication whether the aldehyde was fixed or whether even larger amounts of the corresponding carboxylic acids, formed by atmospheric oxidation, were present.

The tenacity of geraniol was determined as being about 2 days. Fixation with diethyl phthalate gave a value of 3½ days, and with methyl dihydrojasmonate the tenacity was increased to 5 days. The addition of Abitol had practically no effect on the evaporation rate of diphenyl oxide, but with musk ambrette its tenacity could be more than doubled. Doubling of the tenacity was also achieved by fixing 2-hexyl-cyclo-pentanone with methyl dihydrojasmonate. Abitol produced only a 50% increase in tenacity (see Fig. 9).

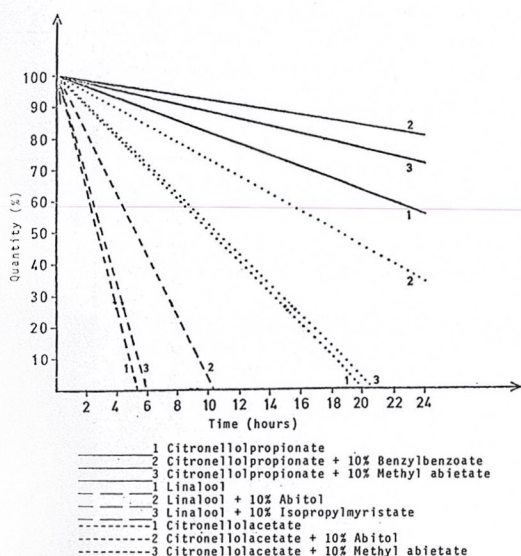


Fig. 7: Fixing of homogeneous aromatic chemicals (up to 24 h).

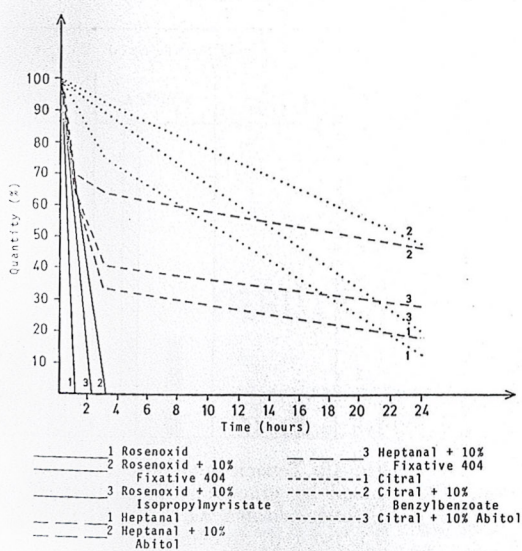


Fig. 8: Fixing of homogeneous aromatic chemicals (up to 24 hours).

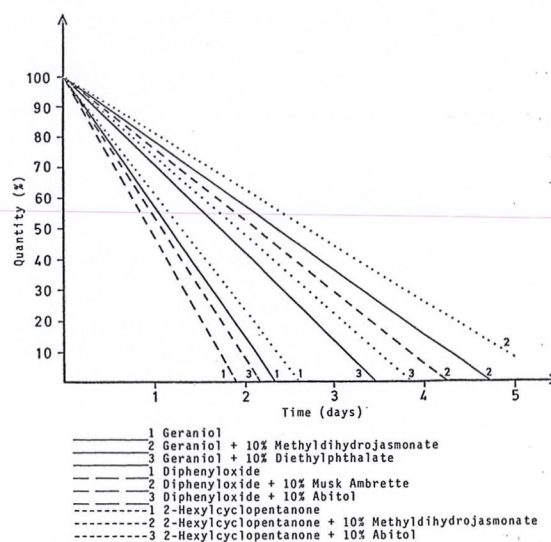


Fig. 9: Fixing of homogeneous aromatic chemicals (up to 5 days).

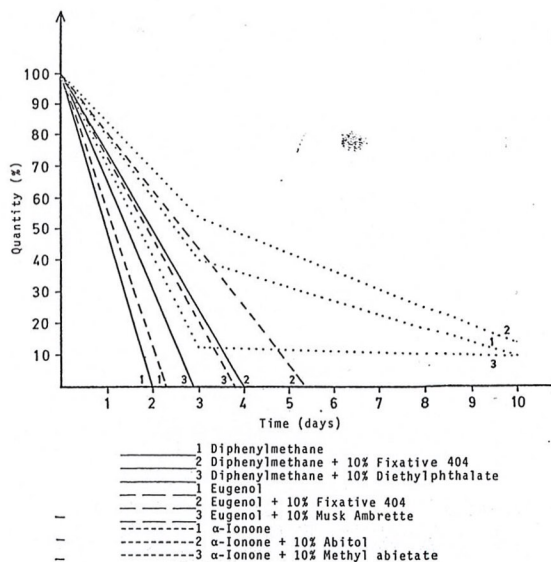


Fig. 10: Fixing of homogeneous aromatic chemicals (up to 10 days).

A clear graduation was also shown by the fixing of diphenyl methane (tenacity ca. 2 days) with diethyl phthalate (3 days) and Fixateur 404 (4 days). The evaporation rate of eugenol was reduced to less than half the unfixed rate by the addition of Fixateur 404, more than doubling the tenacity, whereas musk ambrette caused only a 50% increase in the tenacity (see Fig. 10). In the case of ionone, as in that of the aldehydes, conclusions of practical value could be drawn only with difficulty, because after a few days a residue was formed, which could be measured gravimetrically, but had an odor that differed considerably from the original material. For these materials, the olfactory studies described in the next section yielded usable results.

These experiments showed that the tenacity of any aromatic chemical that evaporated at a uniform rate could, as a rule, be doubled by the use of the most effective of the 8 fixatives studied, and in a few cases the tenacity could be tripled.

	A	B	C	D	E	F	G	H
Ocimen	7	1	5	5	8	5	5	2
Dipentene	6	7	4	4	4	8	4	1
Diphenylmethane	5	7	5	2	8	2	7	2
Linalool	5	8	2	6	8	1	2	2
Tetrahydrolinalool	1	8	5	7	5	3	3	5
Dihydromyrcenol	1	7	5	6	-	3	3	5
Styrolalcohol	7	2	2	7	2	4	7	7
Isopulegol	6	1	6	8	2	4	4	7
Trimethylcyclohexanol	7	2	4	2	4	7	7	7
Benzylalcohol	4	8	2	1	4	4	7	7
Phenylethylalcohol	5	4	8	1	7	2	6	4
Hexanol	7	1	-	6	2	5	3	5
Citronellol	6	2	5	1	8	4	8	3
Geraniol	8	3	5	1	6	2	8	4
Dimethylbenzylcarbinol	3	3	3	6	8	3	7	6
Phenylethyldimethylcarbinol	1	7	4	6	8	4	2	5
m-Kresol	1	7	4	-	6	4	4	4
Eugenol	4	6	4	-	7	2	6	1
Phenylethylisoamylether	1	5	7	8	7	3	4	3
Geranylmethylether	5	7	2	-	6	2	4	2
Rosenoxide	5	6	3	-	7	3	3	3
Eugenolmethylether	6	1	6	-	2	7	3	4
Isoeugenolmethylether	1	3	5	-	4	7	6	2
Diphenyloxide	5	1	4	-	2	6	3	7
Dibenzylether	3	6	7	-	5	4	1	2
Acetophenone	3	2	5	-	1	5	7	7
Cyclohexylcyclohexanone	4	6	2	-	4	2	4	7
2-Hexyl-cyclopentanone	6	1	6	-	3	3	7	3
Dihydrojasmon	3	2	6	-	7	-	6	4
α-Ionone	1	7	4	-	6	4	2	5
Benzylformate	2	1	4	-	7	6	4	6
Phenylethylformate	2	2	5	-	7	3	5	6
Geranylformate	2	2	5	-	5	7	3	5
Decalinolformate	1	2	4	-	3	7	6	6
Nonylacetate	1	4	4	-	4	7	2	7
Isobornylacetate	2	2	6	-	6	6	3	6
Geranylacetate	1	6	3	-	7	4	2	5
Citronellolacetate	1	7	4	-	2	5	3	6
Dimethylbenzylcarbinolacetate	1	2	5	-	3	6	4	7
Citronellolpropionate	1	2	7	-	3	6	5	4
Geranylbutyrate	1	2	6	-	6	4	4	7
Anisylacetate	3	2	5	-	7	2	5	5
Phenylethylisovalerianate	2	6	1	-	7	3	4	5
Isoamylcaprylate	2	6	3	-	7	4	2	5
γ-Octalactone	1	2	6	-	3	4	5	7
Heptanal	3	7	5	-	1	5	3	6
Decanal	1	3	6	-	3	7	5	5
Citral	2	1	7	-	3	5	6	5

A is Abietinsäuremethylester; B is Abitol; C is Benzylbenzoate; D is Diethylphthalate; E is Fixative 404; F is Isopropylmyristate; G is Methyl-dihydrojasmonate; and H is Musk Ambrette.

Table II: Fixation of homogeneous aromatic chemicals.
- = No determination made.

Comparison of the tenacities determined by gravimetric and olfactory methods. To be of practical use, the gravimetrically determined tenacities must be identical or at least parallel to the values determined by olfaction. Figure 11, for example, shows the comparative values for diphenyl oxide.

The tenacities indicated by olfactory testing were less than those measured by gravimetry, but the gravimetric and olfactory values were in the same mutual relation in each case. The olfactory determination of the duration of tenacity also showed that diphenyl oxide could be well fixed by musk ambrette, but scarcely fixed at all by Abitol.

In the case of Rosenoxid the values were identical when the substance was unfixed and when it was fixed with isopropyl myristate. The tenacity of the odorant fixed with 10% of Fixateur 404 was rated considerably higher by olfactory than by gravimetric assessment (see Fig. 12). Apparently small unevaporated amounts of Rosenoxid are very

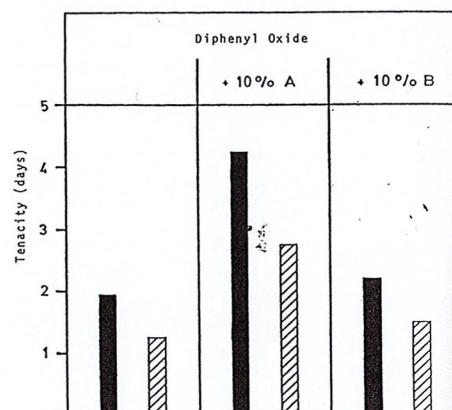


Fig. 11: Tenacities of diphenyl oxide as determined by gravimetry (solid bar) and by olfaction (striped bar). A is Musk Ambrette, B is Abitol.

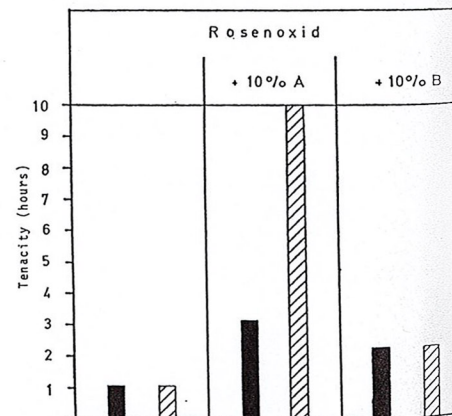


Fig. 12: Tenacities of Rosenoxid as determined by gravimetry (solid bar) and by olfaction (striped bar). A is Fixative 404, B is Isopropylmyristate.

Average ratings

Fixative	Kohlen- wasserstoffe	Alcohol	Phenol	Ether	Ketone	Ester	Aldehyde	*
Abietinsäuremethylester	6.0	4.7	2.5	3.7	3.4	1.5	2.0	3.3
Abitol	5.0	4.3	6.5	4.1	3.6	3.2	3.7	4.0
Benzylbenzoate	4.7	4.3	4.0	4.9	4.6	4.5	6.0	4.7
Diethylphthalate	3.7	4.5	-	-	-	-	-	4.5
Fixative 404	6.7	5.3	6.5	4.7	4.2	5.1	2.3	5.0
Isopropylmyristate	5.0	3.5	3.0	4.6	3.5	4.9	5.3	4.3
Methyldihydrojasmonate	5.3	5.2	5.0	3.4	5.2	3.8	4.7	4.5
Musk Ambrette	1.7	5.2	2.5	3.3	5.2	5.8	5.3	4.8
**	4.8	4.6	4.3	4.1	4.2	4.1	4.2	4.4

* Average rating of fixative over all odorants.

** Average ratings of all fixatives for each class of odorant.

Table III: Fixation of aromatic chemicals containing the same functional group.

- = Not determined.

readily perceptible to the sense of smell.

In the gravimetric measurements, furthermore, the evaporation, especially when at nonuniform rates, was often extrapolated to zero when 1% or 2% of the substance still remained (sensitivity of the balance used).

In the case of citronellyl acetate, the tenacities determined gravimetrically and by olfaction were the same for the unfixed and both fixed samples (see Fig. 13).

In the case of aromatic chemicals that evaporate at nonuniform rates, the endpoint of the tenacity is practically impossible to determine by the gravimetric method, because in these cases the

highly tenacious residue, except in a few cases, has no odorous similarity to the odorant originally used. This is illustrated in Figure 14 for the case of α -ionone. The olfactory test, in contrast, showed that Abitol was a considerably better fixative for α -ionone than was methyl abietate.

In these comparative experiments, the gravimetrically determined tenacities were, for the most part, confirmed by the olfactory determination.

Statistical evaluation. By a purely statistical evaluation, an attempt was made to find, ideally, a fixative that possessed better fixing properties than all the other fixatives tested, or at least to find one fixative



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with optimal effect for each class of substance, for example, for alcohols, aldehydes, or ketones.

Table II summarizes the results of all the experiments on the fixing of homogenous aromatic chemicals. This list gives the most effective fixative in each series 8 or 7 points (depending on the number of fixatives tested) and that with the least effect 1 point. The ratings of the other fixatives are intermediate, according to their effectiveness.

Table III is an evaluation of Table II, showing the efficiency of the different fixatives for odorants containing the same functional group.

For some classes of substance, clear differences were found. Thus, most hydrocarbons, for example, were well fixed by Fixateur 404 and by methyl abietate, whereas musk ambrette had an extremely weak effect. Almost all the fixatives tested were moderately effective with alcohols. Only Fixateur 404 (most effective) and isopropyl myristate (least effective) diverged slightly from the average. With phenols, the best fixing was achieved with Fixateur 404 and Abitol, while methyl abietate and musk ambrette had only slight effects. Since only a few

aromatic chemicals with a phenolic structure were tested, these data should not be overrated. For the most part, moderate effectiveness was also found in compounds containing an ether group. Both benzyl benzoate, the most effective, and musk ambrette, the least effective, had average values that diverged only slightly from the overall mean. Ketones could be well fixed with methyl dihydrojasmonate and musk ambrette, whereas methyl abietate had only a slight effect on these substances. A good rating was obtained by musk ambrette as a fixative for esters, whereas methyl abietate was very poorly rated. Aromatic chemicals containing an aldehyde group were outstandingly well fixed by benzyl benzoate, while methyl abietate had a particularly weak effect on these compounds also.

Reckoned over all the aromatic chemicals tested, scarcely one fixative could be nominated as having particularly good properties, even though Fixateur 404 gained the highest rating. Apart from methyl abietate, which had the least fixative properties by some margin, all the fixatives studied were more or less moderately effective.

Discussion of results

For each of numerous aromatic chemicals, at least one fixative could be determined that possessed good fixing properties for any particular substance. The practical significance of this is that the tenacity of an aromatic chemical can be increased by a not insignificant amount by the addition of a suitable fixative.

Prerequisites for the effectiveness of a substance as a fixative are, among others, a certain molecular size and a vapor pressure lower than that of the odorant to be fixed. The fixing effect is also influenced by viscosity.

From these relationships, it is clear that there is no clear borderline between odorants and fixatives. A good fixative can also have good odorous characteristics, for example, musk ambrette and methyl dihydrojasmonate, and any odorant has a useful fixative effect if its vapor pressure is lower than that of the substance that is to be fixed.

Fixation reduces the vapor pressure of an odorant. As a consequence, its tenacity is increased; of necessity, however, the intensity of its odor will be reduced.

On the basis of the statistical evaluation of the experiments carried out, it was not possible to determine a general relationship between the effectiveness of a fixative, on the one hand, and its chemical structure, vapor pressure, viscosity, molecular weight, dissolving- or absorbing-power, or the structure of the fixed odorant, on the other. Although the effectiveness of a fixative is largely dependent on these material characteristics, it is not possible to state the fixative by which aromatic esters or terpene alcohols, for example, will be particularly well fixed.

In accordance with practical experience, these results also indicate that a perfume oil compounded from numerous odorants with different molecular structures will be better fixed by a mixture of several fixatives than by any single fixative.

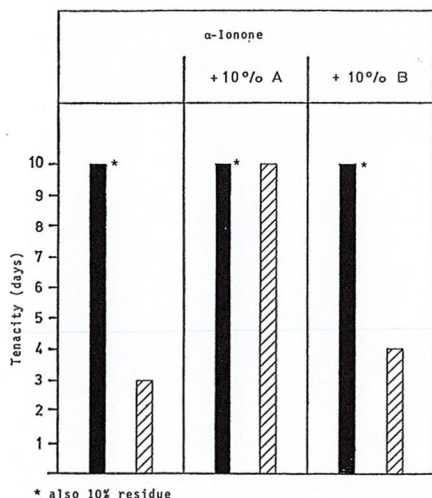


Fig. 14: Tenacities of α -Ionone as determined by gravimetry (solid bar) and by olfaction (striped bar). A is Abitol, B is Methyl Abietate.

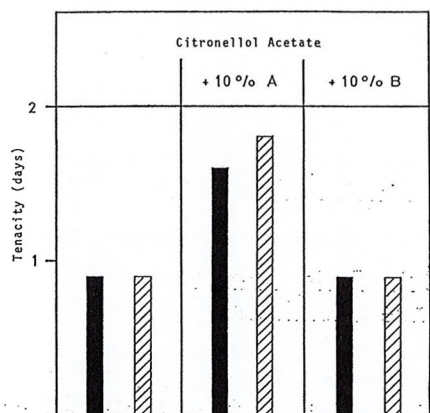


Fig. 13: Tenacities of Citronellol Acetate as determined by gravimetry (solid bar) and by olfaction (striped bar). A is Abitol, B is Methyl Abietate.