New developments for in-can preservation of water-based paints and printing inks

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Summaries

New developments for in-can preservation of water-based paints and printing inks

Water-based paints and most of their precursors must be protected from damage by microbes. The attempts by the paint industry to reduce the amount of volatile constituents have increased the susceptibility to bacterial attack. Consequently, stronger measures have to be taken to improve product hygiene and to optimise the techniques of preservation. Moreover, the selection of preservatives is being increasingly influenced by the Directive on Biocides of the European Union. Examples of recent developments, which will also meet future demands, are represented by products composed of blends of highly active bactericides. Some of these preservation systems, based either on methylol compounds or amines, can be used either to replace or supplement the 5-chloromethylisothiazolinone that is usually used at present. Examples of new developments to meet today's and tomorrow's needs are environmental benign combinations of highly active bactericides. Some preservative systems containing methylol compounds and amines are proposed as a supplement or an alternative to 5-chloromethylisothiazolinone. (5CLMIT).

Nouveaux développements dans le domaine de la conservation en bidon des peintures et d'encres d'impression hydrodiluables

Peintures hydrodiluables et la plupart de leurs constituants ont besoin d'être protégées contre la détérioration provoquée par microbes. Les efforts de l'industrie dont il s'agit à l'égard de réduire la quantité de composés organiques volatils utilisés en peintures et produits assimilés, augmentent-ils la susceptibilité à l'attaque microbiale, et afin de la neutraliser, il est nécessaire d'adopter des mesures de contrôle hygénique et de conservation soigneusement optimisées. Les exigences auxquelles les agents de conservation doivent respectees se changent en raison de la directive sur les produits biocidaux (B.P.D.) de l'Union Européenne. Des exemples des nouveaux développements pour répondre aux exigences d'aujourd 'hui et de demain sont des combinaisons non nuisibles à l'environnement des bactéricides d'haute activité. Certains systèmes de conservation à base des composés méthyloliques et aminiques sont proposés comme supplément ou alternative à 5-chlorméthylisothiazolinone.

Neuere Entwicklungen bei der konsevierung von wasserbasierenden Farben und Tinten

Wasserbasierte Farben und viele ihrer Vorprodukte müssen vor mikrobiellem Verderb geschützt werden. Durch die Bestrebung der Farbenindustrie zur Verminderung der flüchtigen organischen Bestandteile (VOC) erhöht sich die Empfindlichkeit gegen Bakterienbefall. Dadurch müssen verstärkte Anstrengungen zur besseren Produktionshygiene und zur optimierten Konservierung unternommen werden. Dabei wird die Auswahl von Konservierungsstoffen zunehmend durch die Europäische Biozidrichtlinie (BPD) beeinflusst. Beispiele neuerer Entwicklungen, die auch die zukünftigen Anforderungen erfüllen stellen Kombinationsprodukte hochaktiver Bakterizide dar. Einige dieser Konservierungssysteme, die auf Methylolverbindungen oder Amine basieren, können das heute übliche 5-Chlormethylisothiazolinon ergänzen oder ersetzen.

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Introduction

It is indisputable that most water-based architectural paints and printing inks must be protected from microbial spoilage by adding preservatives when produced. The in-can preservation is generally the final step in the development and in the production of a surface coating or an ink. The state of the art for architectural coatings was summarised recently.

As distinct from most other physical or chemical variables in production, which can be controlled immediately, the effects of microbial contamination may not become apparent until it is too late to take effective measurements to keep the product in specification.

The effects of microbial growth in a coating material are well known and are of the same kind as in the daily experience with food; pH-value change, viscosity loss, gassing, malodour, discoloration, visible growth on the surface.

Although added only in small quantities, the preservative confers on the material the necessary stability during storage and transportation until the final use. After the application of the material, either a water-based coating, an ink, an adhesive or other water-based material, the preservative loses its function and does not contribute to the performance of the material. A preservative is added to improve the quality of the product, but only to keep the quality until needed.

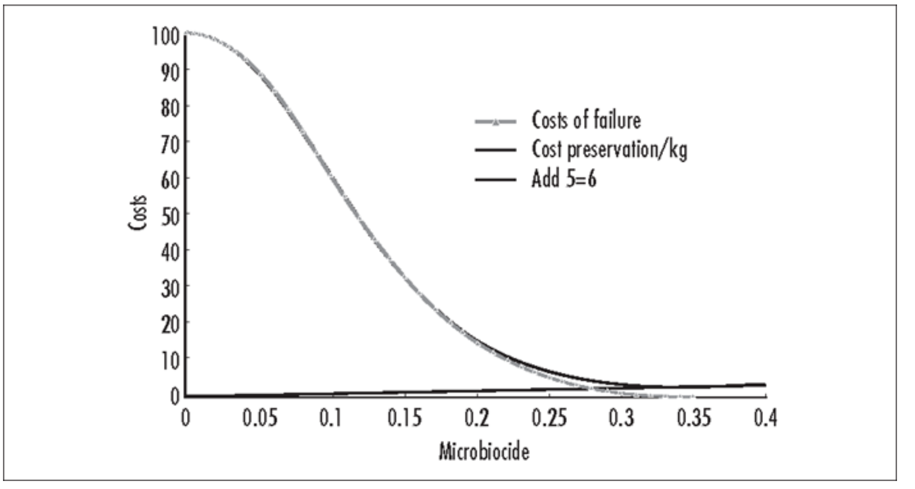

Figure 1: Costs of microbial spoilage and preservation

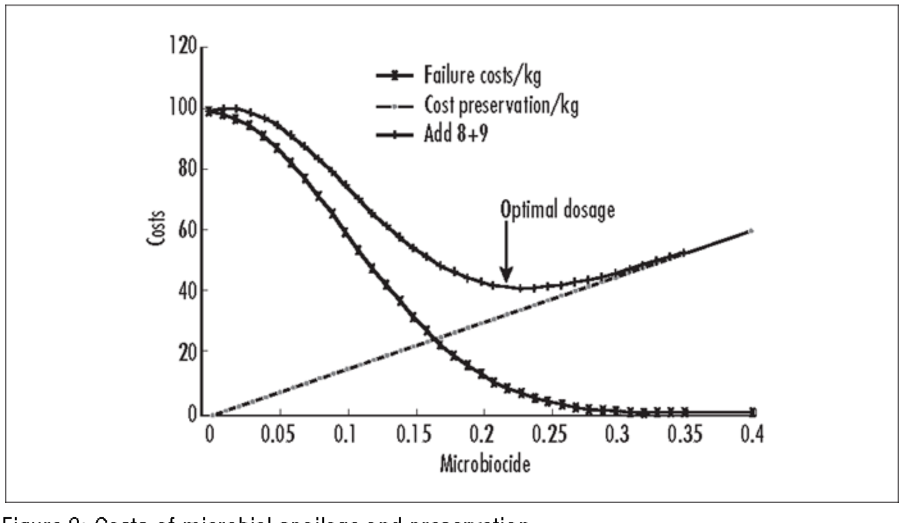

Figure 2: Costs of microbial spoilage and preservation

Cost-efficiency of preservatives

Due to the contribution to the material costs of a paint or ink, it is worthwhile to optimise the preservation. An excessive amount of preservative will automatically result in uneconomic costs, while too low a dosage will inevitably increase the risk of microbial spoilage and only result in even higher costs. It is evident that for a low price preservative the optimisation of the dosage is not of that importance compared to higher priced preservatives. In these cases it is better to add a safe level of the microbiocide. For the high quality microbiocide it is valuable to do laboratory tests to evaluate the optimised concentration. There are other very different additional factors which could make a careful investigation necessary. One example could be the application limits set by authorities for certain active ingredients, compatibility concerns etc.

Not considered up to now are the cost-efficiencies of selection of proper raw materials, improving hygiene conditions in the plant, control of hygiene, improving water quality, hygiene training of the staff. From experience it is well known that costs of measurements to improve the hygiene in the plant pays back quickly. The in-can-preservative cannot correct all the mistakes possible in the plant hygiene.

These are sufficient reasons to know as much as possible about the preservative situation.

In-can preservatives, essential properties

Broad spectrum of microbiological activity

Depending on the conditions in the protected material different types of microbes could cause problems. In an emulsion paint with ph-values of about 8.5 to 9, filled in cans it is normally necessary to prevent the growth of bacteria. In an ink with a pH of about 5, mould growth might cause problems. Other materials such as dyes in wet cake form or polymer emulsions in big storage tanks need different antimicrobial protection against yeasts for example. In contrast to other applications of antimicrobials such as in medicine or plant protection, the micro-organisms that cause the problem are most often not known. Therefore, to prevent any microbiological attack, a broad-spectrum-biocide is best suited.

- broad spectrum of antimicrobial activity
- pH-stability
- temperature stability
- low toxicity
- low ecotoxicity
- compatibility
- easy handling in the production
- cost efficiency

Figure 3: In-can preservatives – Essential properties

pH-Stability

Generally, the biocides used formerly were very stable molecules such as chlorinated phenols or phenyl-mercurials. The more recent ones have a built-in instability to meet ecotoxicological demands, ie, after the in-can preservative has done its job, the activity should cease. Normally this happens by abiotic and biological degradation in the environment. A very important abiotic degradation path is hydrolysis. Of course, in a water-based material, hydrolysis starts immediately after incorporation. By choosing the right biocide for the material to be preserved and for the storage time for which it should be preserved, the pH-instability of a biocide becomes an advantage. If a pH-labile preservative is used, the preservative should be added only at the production stage where the pH is already below the hydrolysis limits. For example, if in paint production the thickeners are prepared at pH 10, 5-chloromethylisothiazolinone-based preservatives should never be added to this point.

Temperature stability

What was mentioned under pH-stability also holds true for temperature stability. In addition to the temperature conditions prevailing during the production of the material, the storage temperature of the preservative itself should be considered. Some of the 5-chloromethylisothiazolinone based preservatives should be stored always below 40°C to prevent degradation even before the preservative reaches the material it is intended to protect. Also, for other biocides some limits in temperature stability exists, for example hydroxymethylformamide gives off carbon dioxide at about 40°C.

Low toxicity

The well known phrase of Paracelsus is still valid today: 'all materials are toxic, but the toxicity is a function of the concentration at which they are applied'. The handling of preservatives is the same as with other chemicals, they can be handled in the plant with the same directions and recommendations as for other chemicals, these can be found on the label of the drum and in the Materials Safety Data Sheet (MSDS). Due to the low dosages, the preservative normally has no effect on the labelling requirements of the goods so preserved.

formaldehyde	• ready biodegradable in diluted solutions
HHT	• ready and completely biodegradable according OECD 301D
chloroacetamide	• completely biodegradable (98%) according OECD 302B
5CLMIT/MIT	• completely biodegradable in diluted solutions
OIT	• ready biodegradable after adaption
oPP	• ready biodegradable after adaption
CMK	• ready and completely biodegradable according OECD 301C

Figure 4: Biodegradability of microbiocides

Low ecotoxicity

Because preservatives are used to kill microorganisms, the products are dangerous for microbes in the environment. As mentioned for the human toxicity the microbiocides lose their activity when diluted below the no-effect-level. The principal route for a preservative to enter the environment is through the waste water treatment plant (WTP). It is important to keep in mind that the elimination of xenobiotics in the WTP is strongly dependent on the adaptability of the bacteria. Bacteria adapt their enzyme battery if faced to non lethal doses of a microbiocide.

Compatibility

The preservative must be compatible in all aspects with a wide range of coating materials and should not influence either the colour, the viscosity or the rheology of the matrix. An important aspect is the reaction of the microbiocide with the constituents in the ink or the paint to be preserved. Especially for the isothiazolinone-based preservatives, even trace impurities in other raw materials can destroy completely the activity of the preservative. On the other hand, other ingredients in a formula can assist to keep below limits the level of free formaldehyde splitting off from a preservative containing formaldehyde reaction products such as the hydroxymethylchloroacetamide.

In polyphasic systems like polymer emulsions or paints, the active ingredient can be adsorbed in non-aqueous phases and are deactivated with this mechanism. Most failures of benzisothiazolinone-based preservatives under neutral or acidic conditions are caused by this mechanism.

Ease of handling in the production

An important property of each raw material is user friendly easy handling in the production. Free flowing pumpable, non-flammable liquids with no aggressive odours are preferred. A very important example is formaldehyde, which is a very aggressive, toxic substance, which can be replaced advantageously by reaction products with amines, alcohols or amides.

For example to store a 37 % formalin solution it needs a heated tank to avoid polymerisation. 1,6-dihydroxy-2,5-dioxhexane with more than 46% bound formaldehyde is a storage stable clear liquid even at 0°C.

Microbial growth in the wet state – Kill rate of preservatives

In principle all the bacteria, yeasts and moulds commonly living in the environment can be found in contaminated inks and emulsion paints. A very big difference to other applications of antimicrobials such as medicine or plant protection is the demand to total control of the different microbes in most technical applications. There is no accepted limit of microbial counts in technical products. Some paint producers ask in their specification for raw materials for 'no bacteria detectable by the means of a ready to use germ-tester'. If slow killing bactericides are used to preserve polymer emulsions after production, the time between production and test of surviving germs should be long enough to give the preservative a chance to act. It was found in practice that polymer emulsions preserved with a 5-chloromethylisothiazolinone based preservative were claimed by the paint producer while a control of the microbial count some days later showed zero bacteria counts.

Of course the speed of kill of a biocide is strongly dependent on the dosage. So a direct comparison of different active ingredients is not straight-forward. It is best to compare standard dosages. It is demonstrated in laboratory tests that the preservatives containing only isothiazolinones as biocides are slowly acting while reaction products of formaldehyde with alcohols, amines and amides gives a high kill rate. Sometimes quick action is necessary to avoid enzyme formation, which can cause viscosity loss by the degradation of cellulose derivatives even after the bacteria faded in the material.

On the other hand, it was found, for example, polymer emulsions with constant viable count of 10^6 germs per ml neither did not change physical parameters over month storage times nor developed any objectionable odours.

5-chloromethylisothiazolinone (5CLMIT)-based in-can-preservatives are the standard systems used today. Characteristics are the very low concentrations of active ingredients used in the products. The actual necessary concentration of the 5-chloromethylisothiazolin-3-one in a matrix is as low as about 10 mg/kg, based on long years experience in Mergal's laboratories. With the known instability against hydrolysis, reducing agents, other reactive species and the slow action against some microorganisms the main issues to improve a preservation system based on 5CLMIT are already considered. The 5CLMIT acts by reaction with essential molecules in the bacteria's life cycle. In competition to this useful reactions with the microbial cells (to inhibit their growth) 5CLMIT is reacting with other constituents in the matrix. In these cases the 5CLMIT is used up without any effect. To ensure product quality it is necessary to prove that the 5CLMIT has fullfilled the job before it is destroyed or otherwise is complemented by a second more stable active ingredient. In the best of the cases a second microbicide stabilises the 5CLMIT in the matrix.

Possible scenarios are:

- The 5CLMIT kills all microorganisms present in closed container; no microbial problem is expected unless the container is not reclosed after partial usage, for example a paint container.
- The action of 5CLMIT is too slow to prevent microbes from producing extra cellulary enzymes which cause viscositiy loss in a paint. The can is sterile when opened but the material lost its function. Addition of an enzyme blocker could improve the situation or the use of a quicker acting microbiocide, like a reaction product of formaldehyde with an alcohol or amide.
- 5CLMIT is destroyed quicker than it acts against the microbes. Either use of different products like amine-based preservatives or combination with stabilising, quick acting microbiocides are indicated.

Stabilisation of 5-chloromethylisothiazolinone (5CLMIT)

It is easily demonstrated by HPLC analysis of 5CLMIT in paints at different pH-values, as well as in buffer solutions, that at pH – values above 8, the hydrolysis is strongly accelerated. While at 30°C and pH=8,5 the half life value of 5CLMIT is counted in months, but at 40°C and pH=9,5 after only one day no more than half of the 5CLMIT survived. Below pH=8 at normal temperature conditions the hydrolyses is negligible. To improve the performance of the biocide it is of great importance to control carefully the pH-value at every production step. Especially alkaline prebatches, such as, for example, preservative plus dispersing agent are to be avoided. Other minor reactive components in the matrix could be reducing agents such as sulphites, amines or other nucleophiles. Even traces from previous production steps can be enough to destroy the 5CLMIT. As exemplified for a no VOC polymer emulsion, often a situation is found where the actual concentration varies from lot to lot. In these cases careful supervision of the production lots is necessary to stabilise the 5CLMIT concentration by controlled production. Especially residues of redox-catalyst systems in polymers or bleaching agents in surfactants are critical impurities.

It is long known that water-based preservatives themselves containing 5CLMIT must be stabilised against decomposition. Effective stabilisers are molecules able to capture nucleophiles and reducing agents. Copper salts are a conspicuous example. In application concentrations the stabilisation by formaldehyde reaction products can be employed. It can be demonstrated that by selection of proper second components, 5CLMIT can be effectively stabilised in applications like paint, polymer emulsions and inks. It is the most effective strategy on a molecular level to stabilise the 5CLMIT by combining the proper amide, or alcohol reaction products with formaldehyde. Also the stabilisers have interesting microbiocidal activity. A very efficient example is the 1,6-dihydroxy-2,5-dioxahexane. Today optimised combined preservatives are commercially available with excellent handling properties.

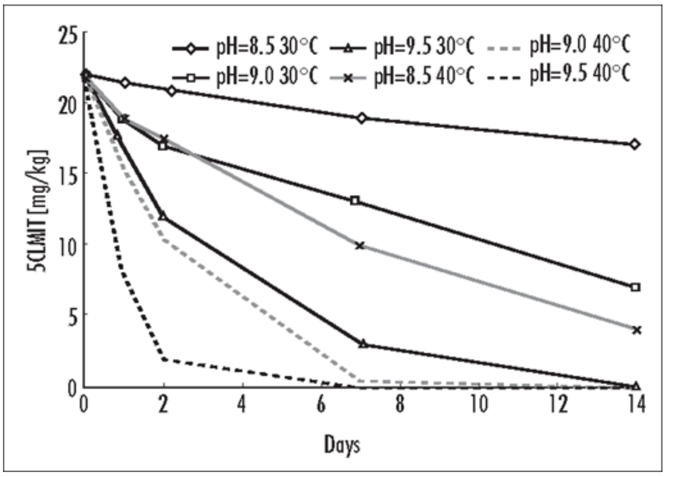

Figure 5: Stability of 5CLMIT in paints pH/temperature

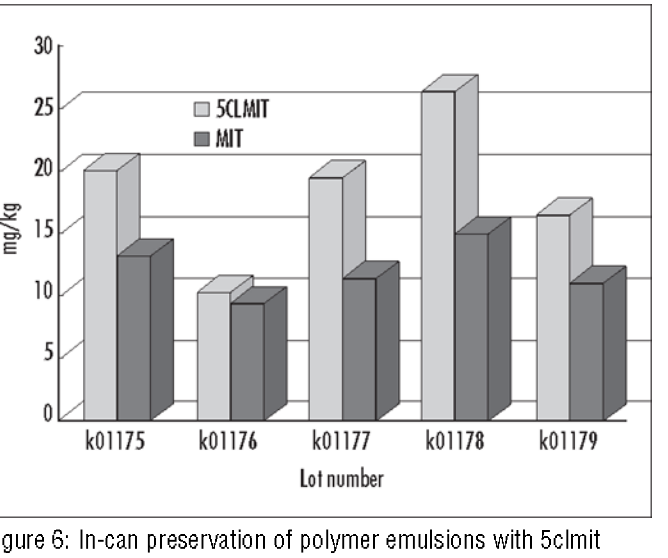

Figure 6: In-can preservation of polymer emulsions with 5clmit analytical process control

Acceleration of 5-chloromethylisothiazolinone's kill-rate

To boost the kill rate of 5CLMIT the combination with the O-methylol or N-methylol compounds is an interesting strategy. Of course an increase in the dosage would speed-up the kill rate, but much less effective. In the laboratory the acceleration by O-methylol compounds (MERGAL K 14 or MERGAL 700K) is higher than with N-methylol (MERGAL K6N, containing hydroxymethylchloroacetamide). Amine-based preservatives such as, for example, 4,4-dimethyloxazolidine or 1,3,5-trishydroxyethylhexahydrotriazine, show high kill speed, but combined formulations with 5CLMIT are not available.

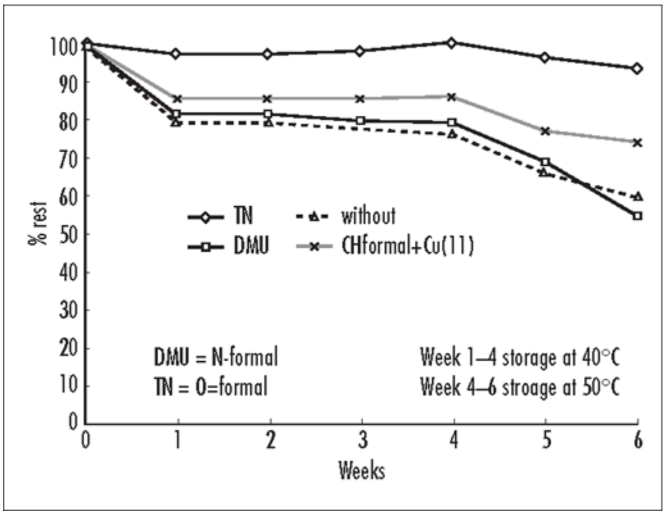

Figure 7: Stabilisation of 5CLMIT at pH 8.5 by an additive

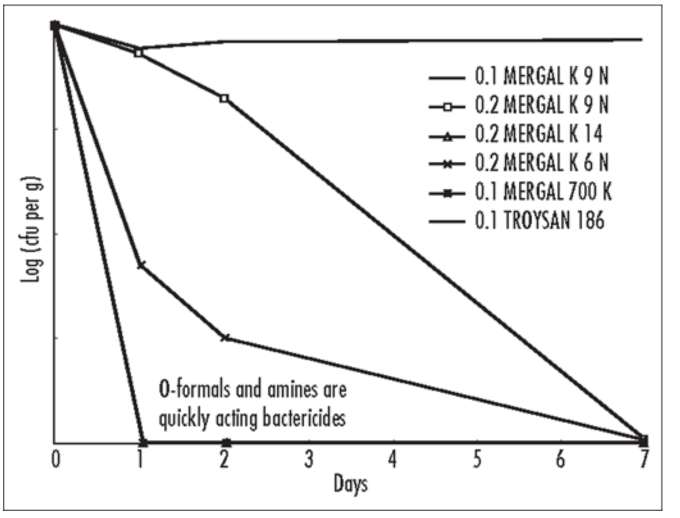

Figure 8: The speed of kill of in-can preservatives

Alternatives to 5-chloromethylisothiazolinone-based preservatives

In respect to the discussed instability and the known skin sensibilisation properties of the 5CLMIT-based products, there is an interest in alternative methods of preservation. The O-methylol and N-methylol compounds already discussed give an important potential for the reduction of applied 5CLMIT dosages.

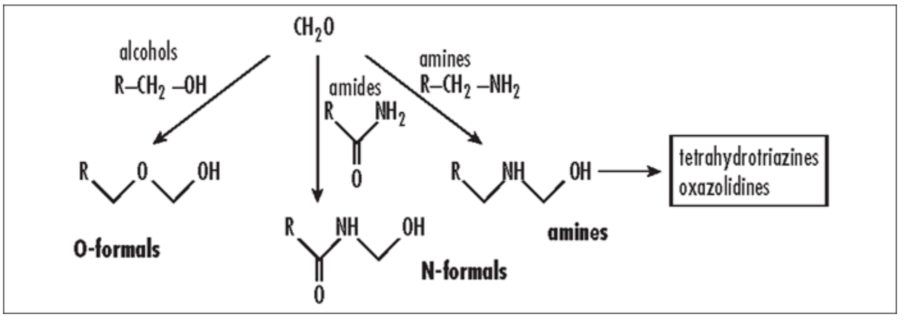

Figure 9: Formaldehyde reaction products of alcohols, amides and amines

The limits are the hydrolysis to formaldehyde in diluted water-based matrices.

The hydrolysis could be demonstrated by NMR-techniques for the risk evaluation of such compounds, hydrolysis is a welcome process because the products of hydrolysis are well investigated compounds. It was shown that in an emulsion paint the addition of a reaction product of formaldehyde with an alcohol or amide containing 100 mg/kg of formaldehyde in the can did not split off formaldehyde into indoor air above the recommended limits of the BgVV (German Federal Institute for Consumer Health and Veterinary Medicine, Berlin) for living rooms.[1,4]

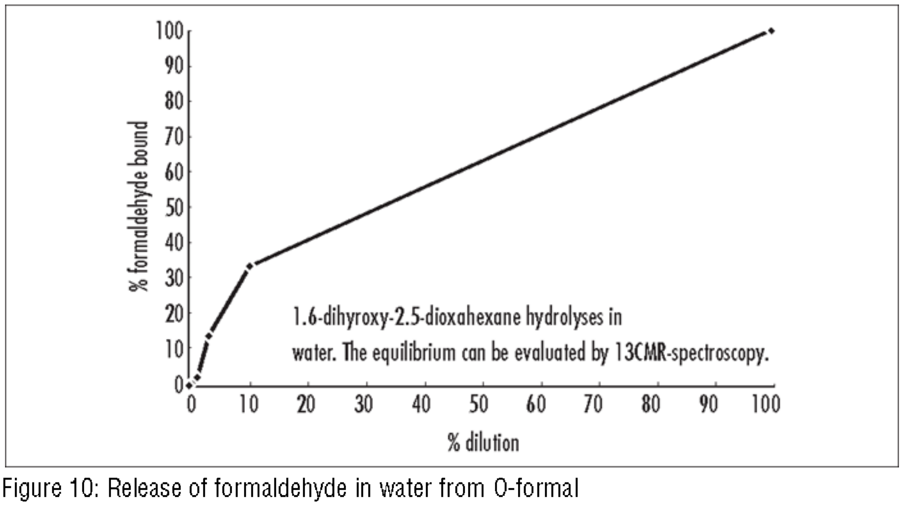

Figure 10: Release of formaldehyde in water from O-formal

To widen the activity range of an O-methylol or N-methylol compound the low toxic microbiocide 3-Iodopropinoxybutylcarbamate (IPBC) can be applied. A synergistic effect of the components was demonstrated. The combination of the selected N-methylol compound 1,3-Dimethylol-5,5-dimethylhydantoin (DMDMH) with IPBC is a well accepted system for the cosmetic industry and should now be considered as interesting alternative preservative for inks, paints and other coating materials.

Amine-based preservatives are a class that should be considered as cost effective alternative to the isothiazolinones. The reaction products of formaldehyde and amines have been used successfully for more than 25 years.

The products are stable in alkaline media such as emulsion paints and do not behave as formaldehyde donors. In a series of experiments to determine emission factors from a standard vinyl acrylic interior wall paint in small-scale chambers it was demonstrated by Mookherjea and Colon,[2] that the unpainted wallboard used as a support also releases some formaldehyde into the indoor air. Painting the wall board with an unpreserved paint reduced the formaldehyde emission in the test chamber. The amine-based preservatives were applied at the highest recommended dosages as worst case conditions. A modelling was performed with the data for a typical room and ventilation rates with air changes per hour ranging from 0,2 (enclosed room) to 2 (open window).

In the worst case 82 ppb formaldehyde was the highest indoor air concentration emitted from the preserved paint. In all cases that involve paint drying, a maximum amount of formaldehyde

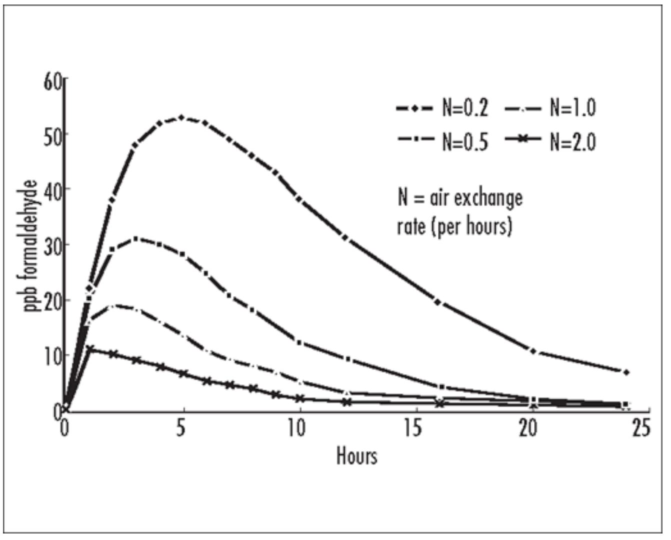

Figure 11: Formaldehyde emissions – wall-board painted with paint containing 0.2% truysan

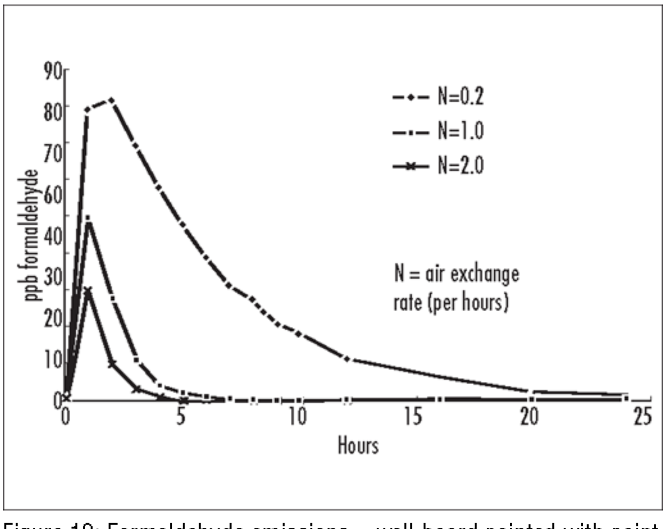

Figure 12: Formaldehyde emissions – wall-board painted with paint containing 1.2% truysan

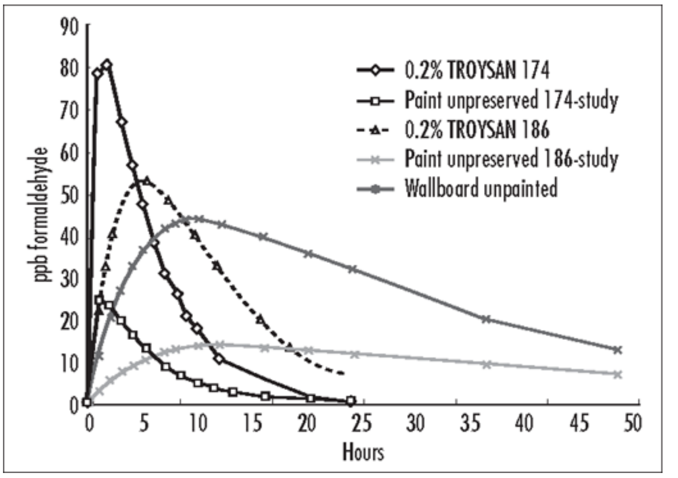

Figure 13: Formaldehyde emissions – wall-board ventilation: air changes per hour N=0,2 (well-closed room)

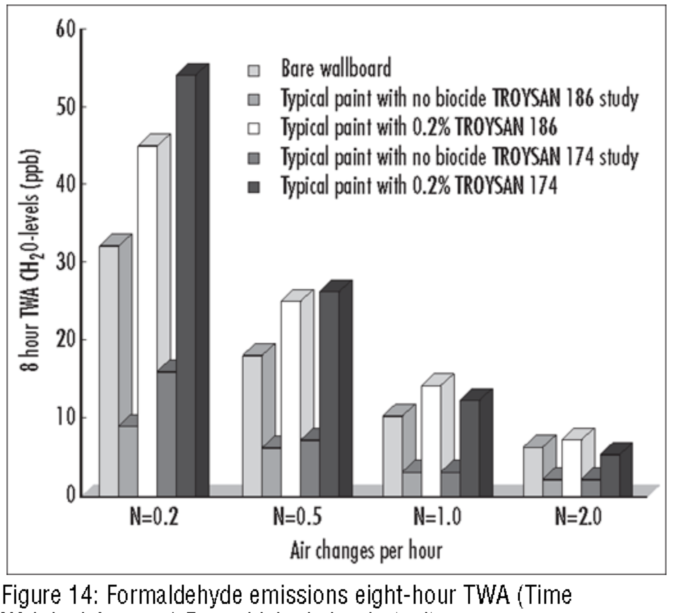

Figure 14: Formaldehyde emissions eight-hour TWA (Time Weighed Average) Formaldehyde levels (ppl)

corresponded to the water that evaporated from the paint, and generally after about 24 hours, levels were below 10 ppb even with very poor ventilation. In every case it could be demonstrated that the room ventilation is the most effective means of decreasing quickly air concentration of formaldehyde quickly. The emission characteristic of the wall-board is a very important factor in the estimations. Formaldehyde emissions from an interior paint are of no matter for the users of the painted rooms.

Eight hours time-weighted average formaldehyde levels are calculated from the experiments. Even under the worst case conditions the 100 ppb OSHA (Occupational Safety and Health Administration, US Department of Labor) limit was not exceeded.[3]

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