Reduction of formaldehyde in ambient air through application of special acrylic co-polymer in paint-and-lacquer coatings

R F Runova¹, V V Pipa¹, Yu L Nosovsky¹, M A Laboda² and I B Monfort³

¹Department of Technology of building constructions and wares, Kyiv National University of Construction and Architecture (KNUCA), Kyiv, Ukraine
²Department of Raw Materials for Coatings, Dry Building Mixes and Adhesives, Group of Companies LKB LLC, Kharkiv, Ukraine
³Technical Group Architectural Coatings, EMEAI Dow Coatings Materials, Dow Europe GmbH, Horgen, Switzerland

pipa.volodymyr@gmail.com

Abstract. Application of modern coatings in interior decoration is becoming increasingly popular. With their help, new decorative effects are created and implemented, which contribute to the desired aesthetic pleasure. The development of the chemical industry allows to produce a wide range of decorative coatings, paints and water-based enamels, as well as other finishing building materials that are widely used by designers and craftsmen in the design of premises. As a result, manufacturing companies face a clear challenge in creating safe materials for human health. It is known that the use of preservatives, plasticizers and opalescent additives in coatings are a source of harmful volatile organic compounds (VOCs), in particular phenol-formaldehyde resins, which provoke dangerous human diseases, and formaldehyde itself (H₂-C=O) is a carcinogen and can cause lungs, nasopharyngeal cancer and cause acute myeloid leukemia. Formulation models of coatings based on PRIMAL™ SF-208 ER acrylic copolymer dispersion have been developed, which, among the required operational and quality characteristics, have the ability to reduce the content of formaldehyde. There is defined the regularity of the increase in the amount of phenol-formaldehyde absorbed by the paint from the ambient air from the increase in the quantitative content of the dispersion in the paint.

1. Introduction

There are more and more challenges that threaten human life and health today than ever before. We are not insured against some dangerous influences, but it is quite possible to avoid danger due to the introduction of modern scientific knowledge in production technologies.

It is known that about 90% of the time city dwellers spend in residential and office premises, the level of air pollution in which is several times higher than in the open air. Not least because the main source of contamination are building materials and paints, which may contain phenol-formaldehyde resins [1] \([C_6H_5(OH)-CH_2-]n\) – macromolecular compounds formed by the interaction of phenol \(C_6H_5OH\) with formaldehyde (H₂-C=O) in the presence of acids (HCl, etc.) or alkalis (NaOH, NH₄OH) as catalysts [2]. Both formaldehyde and phenol used in the production of phenol-formaldehyde resin [3] are toxic and flammable substances. Phenol-formaldehyde resin has a negative effect on the human body: it causes eczema and dermatitis. Chronic formaldehyde poisoning can be manifested by loss of appetite, weight loss, weakness, persistent headaches, palpitations, insomnia. But most importantly, formaldehyde H₂-C=O according to the IARC (International Agency for Research on Cancer)
2. Analysis of Recent Research and Publications

According to the Directive 2004/42/EC of the Council of European Parliament dated April 1, 2004, phenol-phomaldehydes are also volatile organic compounds (VOCs) [5] and subject to certain restrictions.

It is known that in the production of water-soluble paints, which include primers, putties, decorative coatings, paints, enamels and decorative plasters for facade insulation systems (ETICS), as the main binder are polymer dispersions, which can be platoon -polymers by main types of origin: acrylic, styrene acrylic, styrene butadiene, vinyl acetate, the most common of which is styrene acrylic copolymer [6].

One of the most important indicators of the quality of such co-polymer dispersions is the minimum temperature of film formation (MFFT). To form a film from the dispersion that is part of the paint, it is necessary that the drying temperature was higher than the MFFT [7]. If the drying temperature is lower, it will lead to irreversible coating defects. As a rule, dispersions traditionally have MFFT + 8 °C to 22 °C. To reduce the MFFT, paint manufacturers traditionally use external plasticizers, or organic solvents, which are also called film-forming additives, or opalescent agents [7], which after the end of their action to create a film evaporate, forming a non-stick surface. Despite the fact that they are inert to solutes, plasticizers are able to penetrate the human body in the form of evaporation through the skin, mouth and lungs. Another source of formaldehyde is container preservatives, which traditionally contain either free formaldehyde or its donors.

Socially responsible companies, understanding the future and importance of safe products, are already working to improve materials to reduce the content of harmful substances. For example, DAW SE (Germany) has developed and launched three lines of E.L.F. plus (Emissions- und Lösemittel-Frei®, which means without solvents and harmful emissions plus without preservatives) – interior paints, primers and plasters [8].

As for the US market, American scientists, for example, have developed an interesting technology for the production of so-called ceramic coatings. Ceramic wall paint is a fairly recent alternative to traditional water-based paints. These paints are based on acrylate binders and are not only high strength, but also low VOC content. Ceramic paint acquires its characteristics due to the tiny ceramic "beads" used as pigment fillers. These "beads" have a tiny size and a perfect cylindrical shape and due to this pigment filler, there is formed a perfectly smooth coating with very high resistance to wet abrasion [9].

For example, the Michigan company O'Leary Paint, along with some other manufacturers, offers a line of premium enamels "Ceramic Coat Interior Premium", which uses the above-mentioned technology of ceramic paints [10].

In addition, recent studies on the development of modified phenol-formaldehyde resins indicate a decrease in the content of free formaldehyde [11].

It should be noted that some Ukrainian companies are already working to reduce phenol-formaldehyde in coatings. So, KOMPOZIT™ worked to create such a paint "PRIME AIR" [12].

3. Purpose and Tasks

Taking into account the successful experience of global companies in VOCs reduction in coatings that limit the content of plasticizers, coalescents and container preservatives, it is proposed to create working models of formulations for semi-gloss and matte coatings. When developing such formulations, avoid the use of coalescents and container preservatives. The coating must meet quality requirements and be able to absorb formaldehyde present in the ambient air.

4. Raw Materials and Methods

PRIMAL™ SF-208 ER acrylic co-polymer dispersion from DOW Chemical was used as a binder [13]. This dispersion is designed to create paints in response to growing concerns about indoor air quality (IAQ-Indoor Air Quality) and the health effects associated with exposure to formaldehyde. The dispersion does not contain alkylphenol ethoxylates (APEO-free) [14] and when developing coatings using it does not require the introduction of coalescents, as the MFFT is 4°C. The properties of coatings
made of this material allow you to independently form a film, which during operation provides irreversible binding of formaldehyde to the indoor air, thus making it safe. The main properties of the dispersion are given in (table 1).

**Table 1. Basic properties of PRIMAL™ SF-208 ER dispersion**

| Property                        | Typical Values       |
|---------------------------------|----------------------|
| Appearance                      | Opaque, white to off-white liquid |
| Solids, by weight, %            | 48                   |
| pH                              | 8.8                  |
| Viscosity (Brookfield, LV 2#, 60 rpm, 25°C), cps | <500                |
| Minimum Film Forming Temperature, ±2°C | 4                   |
| Density (g/ml), wet             | 1.06                 |
| Storage precautions             | Protect from freezing|

The principle of action of the dispersion film is the absorption of functional monomers of carbon and hydrogen from formaldehyde and their return to the air in the form of water vapor.

In this work, field tests were performed according to the methods of DOW Chemicals, in order to determine the properties of the coating to absorb formaldehyde.

Static and dynamic testing methods were used to determine the formaldehyde content. The essence of the static method was to use a room with the same properties, which remain unchanged (table 2). The formaldehyde content was checked using a Formaldegidmeter hV. The equipment of this type allows to perform measurements in a wide range and with sufficient accuracy quickly enough, in 60 ÷ 180 sec.

**Table 2. Characteristics of the room for determination of the content of formaldehyde by static method according to the method of DOW Chemicals**

| Room characteristics | Manager office |
|-----------------------|----------------|
| Room type             | Manager office |
| Room description and its components | The walls made of ceramic block and mineral plaster. Lightweight concrete and laminate floor. Ceiling made of reinforced concrete and mineral putty. Aluminum profile window. |
| Possible source of formaldehyde | Doors and furniture made of MDF plates. Polyurethane plinth, vinyl glue |
| Room volume           | 31.4 m³         |
| Total area of surfaces (walls, floor, ceiling) | 50.9 m²         |
| Total area of window and door | 3.2 m²         |
| Painted area          | 10.3 m²         |

Samples of semi-gloss and matte coatings, in the amount of 7 kg each, were prepared with the help of laboratory dissolver DISPERMAT® CN20 with the same dosing and dispersing regimen. The composition of the formulations is shown in (table 3).

**5. Results and Discussion**

Measurements were performed by simulating two types of conditions. In the first case, the window and door were closed, and in the second case, the window was periodically opened for ventilation. The measurement results are shown in Figures 1 and 2.
### Table 3. Paint formulations for formaldehyde abatement testing

| Recipe code       | VP12/19 | VP15/19 | VP18/19 | VP21/19 |
|-------------------|---------|---------|---------|---------|
| **Component, kg/to** |         |         |         |         |
| Water             | 183.79  | 194.65  | 220.89  | 216.33  |
| BYK-024           | 1.96    | 1.98    | 1.64    | 1.63    |
| Orotan 731AER     | 12.79   | 12.87   | 21.21   | 21.19   |
| Acrysol RM-5000   | 33.47   | 23.99   | 33.86   | 31.25   |
| Tioxide TR 92     | 178.97  | 178.92  | 281.66  | 280.55  |
| Minex S6          | 153.27  | 152.56  | 262.88  | 259.24  |
| Primal TM SF 208 ER| -       | 426.80  | -       | 157.17  |
| Usual acrylic dispersion | 414.75 | -       | 161.06  | -       |
| Acrysol TM RM-8W | 20.00   | 7.23    | 16.00   | 31.84   |
| RocimaTM 564      | 1.00    | 1.00    | 0.80    | 0.80    |
| **Total, kg**     | 1000    | 1000    | 1000    | 1000    |
| **Density, gr/m³**| 1.34    | 1.34    | 1.61    | 1.61    |
| **PVC, %**        | 37      | 37      | 72      | 72      |
| **VS, %**         | 38      | 38      | 38      | 38      |

*a Reproduction of formulation is possible under conditions of observance of a certain sequence of dosing of components, a mode of turns of a mill and time of dispersion.*

![Diagram](image-url)

**Figure 1.** Static method in closed room
As can be seen from the diagram (Figure 1), the concentration of formaldehyde has decreased by more than 20% since the third day. The dynamics of the measurement within 29 days from the moment of coating shows that formaldehyde can be absorbed in the amount of more than 32% compared to conventional paint.

The results of formaldehyde measurements in a ventilated room (Figure 2) are somewhat different and indicate a decrease in concentration by 50%.

Dynamic tests were performed with the help of photoelectric photometry method according to the requirements of DIN EN 482:2015 [15], EN 689:2018 [16] and NIOSH Formaldehyde Method No.2016 [17]. For this purpose, models of the rooms were made, which were painted with the above-mentioned samples of paints. The FP-31 gas analyzer (“Tritech Instruments”) was connected to them by probes. The research results are shown in (table 4).

**Table 4.** The results of the study for determination of formaldehyde by the dynamic method

| Property of paints | PVC =37%, VS=38% | PVC =72%, VS=38% |
|-------------------|-------------------|-------------------|
| Type of binder    | Usual acrylic dispersion | SF208ER |
|                   | VP12/19           | VP15/19          |
|                   | Usual acrylic dispersion | SF208ER |
|                   | VP18/19           | VP21/19          |
| H2−C=O concentration the lower, the better |
| 2 hours           | 68 μg/m³          | 17 μg/m³         | 83 μg/m³         | 14μg/m³      |
| 48 hours          | 88 μg/m³          | 35 μg/m³         | 85 μg/m³         | 33 μg/m³      |
| H2−C=O reduction the higher, the better |
| 2 hours           | 19%               | 82%               | 9%               | 87%          |
| 48 hours          | 2%                | 61 %              | 6%               | 69%          |

According to the results, it can be concluded that semi-gloss coatings, which were made on the basis of PRIMAL™ SF-208 ER dispersion give a significantly lower concentration of formaldehyde – 4 times in two hours and 2.5 times in 48 hours. Regarding the reduction percentage, the results indicate an intensive process of formaldehyde absorption by the coating film and its neutralization. A similar effect occurs when testing matte paints, but in contrast to semi-gloss, where the content of acrylic co-polymer is much higher, this manifestation is not the same, although quite significant in comparison with traditional paints.
6. Summary
Basic formulation models of semi-gloss and matte coatings were created without the use of coalescents and container preservatives. The measurement results suggest that the obtained coatings are able to absorb formaldehyde from the surrounding air and neutralize it. The test results coincide with the experimental data from DOW Chemical. Their analysis provides grounds for further implementation of the Primal™ SF-208 ER dispersion in the field of paint coatings and further study and research of the possibilities of reduction of formaldehyde in paints and coatings for both internal and external use. It is established that when increasing the amount of co-polymer in the formulation to 43%, with the pigment volume concentration (PVC) in the range of 35-40%, the coating has the ability to remove more formaldehyde than in case of matte paint, where the polymer concentration is 16%, and PVC is 72%. Thus, semi-gloss paint in the amount of 1 gram can remove up to 1.34 mg (H₂–C=O) from 1 m³ of air compared to 1 gram of matte paint, which can remove only 0.53 mg (H₂–C=O).

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