Novel alkyd-linseed oil emulsion formulations for wood coatings

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Abstract. In this experiment an oil-in-water emulsion, suitable as a coating for wood surface protection, was obtained. The main components of this emulsion were linseed oil and an alkyd, mixed at a ratio of 1:2. The experiments were conducted to find a valid combination of solubilizing agents, capable of giving a stable emulsion. Several surfactants, obtained from different producers, were tested. The main factors considered were the nature of the surfactant and its hydrophilic-lipophilic balance (HLB). Our results confirmed that the most suitable surfactants were ethoxylated non-ionic types with a high HLB value, while surfactants based on the gemini technology showed a poor efficiency due to scarce solubility in water, which led to the separation of phases. Once the optimal emulsion composition was obtained, hydrothermally treated and untreated aspen wood samples were coated to evaluate the degree of coating absorption for two different substrates.

Introduction

To protect wood and to improve its appearance and service life, coatings have been used for many centuries. Still today, they occupy a prominent position in the market of wood finishing, and their offer is very wide. Coatings can be distinguished according to the chemical composition of the binder: acrylic, alkyd, polyurethane, nitrocellulose; the destination of use: indoors or outdoors; the nature of solvent, etc. The required properties and, consequently, the formulation of wood coatings commonly depend on the end-use sector: either indoors or outdoors [1]. Coatings can provide wooden materials with the desired aesthetical properties, but are mostly of vital importance in the protection of wood against environmental influences responsible for the deterioration or damage of mechanical or chemical origin. This applies to both interior and exterior applications [2]. When exposed outdoors, wood is subjected to a set of stress factors like light irradiation, thermal radiation, mechanical impact, moisture change and biological attack, causing different weathering effects: photochemical and biochemical degradation, mechanical damages to the surface and colour changes [3]. Coatings for interior use also must withstand different degradation factors like light, climatic variations, mechanical damage like scratches, abrasion, impact and chemical interactions, though conditions are not so harsh like in outdoor exposure: interior wood products require less protection against water and UV radiation than exterior wood products, and finishes usually last for decades [4]. Historically, solvent-borne chemistries dominate wood coatings technologies, and still nowadays, industrial coatings are mainly solvent-borne formulations. However, in the last 20 years, due to the environmental legislation and economic constraints, manufacturers of coatings, ink and adhesives have come under increasing pressure to reduce or eliminate the content of volatile organic compounds (VOC) and hazardous air pollutants (HAP) from formulations, because of the hazard they represent to the environment and the human health [5]. In Europe, this is stated by the Directive 2004/42/EC of the European Parliament and of the Council of 21 April 2004 on the limitation of emissions of volatile organic compounds due to the use of organic solvents in decorative paints and varnishes, amending the already existing Directive 1999/13/EC (“the Paints Directive”). As a result, formulators and users of industrial coatings now face significant challenges as they try to respond to their customers’ demands for cost-effective, high performance...
paints and coatings while meeting increasingly stringent regulations. Actually, there are three leading alternative technologies: water-borne, powder and radiation curable coatings. These relatively new technologies must be improved to keep up with the results of appearance and performance, obtainable by using the solvent-borne technology. Therefore, a continuous improvement of formulations is necessary in the coatings industry in order to satisfy the increasing requirements. In our study, we investigated new formulations for a water-borne coating, using alkyd and linseed oil as binders. Alkyd resins are condensation polymers derived from polyols, a dicarboxylic acid or carboxylic acid anhydride and fatty acids. The name “alkyd” comes from its ingredients; ALcohols and aCIDs, where lately the part CID was replaced with KYD, and the term “alkyd” was created. These resins are polyesters modified with monobasic fatty acids. Alkyds are fundamental binder materials for the manufacture of different types of surface coatings. Alkyd based coatings have good surface coating properties such as good corrosion protection, high gloss, fast dryness, and these resins have good interactions with polar substrates such as wood and steel [6]. Before the introduction of alkyd resins, natural vegetable oils had been used in wood finishing, among them linseed, tung, soybean and safflower oils: they contain unsaturated fatty acids and through a chemical reaction, the oil components crosslink by the action of oxygen, forming a solid film; hence, the definition of drying oils. The most used drying oils are linseed and tung oils. Linseed oil contains unsaturated fatty acids such as linoleic and linolenic acids. it is a relatively inexpensive resource for drying oil, and it provides good protection of wood where the penetration ability of the oil into the wood is superior to other alternatives. However, there are disadvantages such as problems of yellowing, poor long-term stability and rather soft films [7]. This has been the major reason for the replacement of linseed oil by modern synthetic coatings such as alkyds and latex coatings in wood protection; however, linseed oil still plays a role in contributing to the properties of coatings like gloss and elasticity; in wood coatings’ formulations, it can be added to alkyd resins. The aim of this study was to obtain an oil-in-water emulsion, suitable as a coating for wood surface protection.

Materials and methods
Composition of the coating

The main components of the emulsion we tried to obtain were distilled water as a solvent, binders and surfactants. Only water was used as a dispersing agent, without a cosolvent, that is usually present also in water-borne coatings. The binders used in this study were linseed oil and alkyd resin they were provided by the Riga Varnish and Paint Factory. Alkyd was prepared heating 55% of tall oil fatty acids, 25% of phthalic anhydride and 20% of pentaerythritol; as a result, a medium length alkyd was obtained. The content of alkyd and linseed oil in the emulsion was about 20%, and their ratio was 2:1, respectively. Samples of 9 surfactants were provided by the Air Products Company; they were selected according to their chemico-physical properties and as recommended by the producer for use in water-borne coating formulations. Their generic characteristics are listed in Table 1. The concentration of the surfactant varied between 1.5% and 2.5%. The Carbowet series surfactants are linear ethoxylated alcohols, with a chain length varying from 9-11 (Carbowet 109, 125, 138) to 12-15 atoms of carbon (Carbowet 144), the Dynol and Surfynol series are acetylenic based surfactants, all containing a triple bond: Dynol 800 and 810 are the same ethoxylated 2,5,8,11-tetramethyl-6-dodecyn-5,8 diol, but at 2 different concentrations, Surfynol 104A is a solution of 50% 2,4,7,9-tetramethyl-5-decyne-4,7-diol in 2-ethylexanol, Surfynol 440 is ethoxylated 2,4,7,9-tetramethyl-5-decyne-4,7-diol, and Surfynol 2502 is ethylene oxide-propylene oxide copolymer diether with 2,4,7,9-tetramethyl-5-decyne-4,7-diol (all surfactants of the Surfynol series are derived from 2,4,7,9-tetramethyl-5-decyne-4,7-diol). The concentration of the surfactants was between 1% and 2%. Other additives were included in the formulation: cobalt drier to promote the oxidative reaction of binders, an anti-skinning agent to complex cobalt drier, thus avoiding top film formation during storage, and an antifoam agent to prevent foam formation during the emulsification process.
Table 1.

Surfactants used and some of their characteristics

| Name of surfactant | Type-concentration (%) | HLB | Aspect       |
|--------------------|-------------------------|-----|--------------|
| Carbowet 109       | Nonionic, 60-100        | 13.1| Liquid       |
| Carbowet 125       | Nonionic, 100           | 12.5| Liquid       |
| Carbowet 138       | Nonionic, 100           | 13.9| Liquid       |
| Carbowet 144       | Nonionic, 100           | 14.4| Solid wax    |
| Dynol 800          | Nonionic, gemini, 70    | not available | Liquid     |
| Dynol 810          | Nonionic, gemini, 80    | not available | Liquid     |
| Surfynol 104A      | Nonionic, gemini, 50    | 4   | Liquid       |
| Surfynol 440       | Nonionic, gemini, 100   | 8   | Liquid       |
| Surfynol 2502      | Nonionic, gemini, 100   | 8   | Liquid       |

Preparation and testing

To facilitate the emulsification, a high shear is necessary, since water and the binders are immiscible. The components were mixed using an ultrasonic homogenizer MRC Sonic-650, with a power of 650 W, set at 70% of total power. Total mixing time was 10 to 20 min; it consisted of repeated sessions of mixing and pauses – 9 s of mixing, followed by 1 s of a pause, respectively. The homogenizer measured the temperature of the sample and to avoid the heating of the emulsion; a bath of ice and water was necessary to keep the temperature low. To verify the drying rate and measure the solid content, 2 g of coating was put in an aluminium plate and let it dry at room temperature, measuring the weight after 24 and 48 h. Coating tests were conducted on samples of aspen (*Populus tremula*) measuring 150x70x15 mm, to verify the applicability and penetration of the coating. Three layers of coatings were applied with a brush, allowing each layer to dry for 24 h. To verify the response of different substrates, coatings were applied on hydrothermally treated and untreated samples. The hydrothermal treatment has influence on the chemico-physical properties of the wood, in particular it decreases its equilibrium moisture content (EMC) and its density; after conditioning hydrothermally treated and untreated samples at a moisture of 65%, the EMC is 4.6% and 10.7% respectively for treated and untreated aspen wood samples. Also a decrease of density was observed; untreated aspen has an average density of 0.524 g/cm³, after the hydrothermal treatment density decreases to 0.445 g/cm³, thus becoming lighter and more porous; this is due to the loss of mass after thermal degradation of wood components. The difference in density can affect the penetration of coating. Aspen wood was hydrothermally treated at 170°C for 100 min at high pressure in water vapour medium.

Results and discussion

Emulsification of alkyd and linseed oil

All water-borne coatings need surfactants in order to reduce the free energy of the various interfaces of the system, thus providing kinetic stability to the formulation. Surfactants cover a wide range of functions in coatings – they allow the emulsification of binder in the solvent, facilitate dispersion of
pigments, they are needed to improve wetting on low energy substrates, to control foaming during the application and processing, and to prevent film defects, caused by surface tension gradients [8]. The first step was the choice of the right surfactants, among the available ones, to emulsify the binders initially without other additives. Our experiments confirmed that the most suitable surfactants are those of the Carbowet series, ethoxylated alcohols: they are nonionic, with a high HLB, are easily and totally soluble in water, and form stable oil-in-water emulsions with alkyd and linseed oil. Emulsification of alkyd and linseed oil with other surfactants, Dynol and Surlynol, was not successful, due to the separation of phases that rapidly occurred after mixing. Though gemini surfactants have a higher surface activity, owing to their structure, containing two hydrophobic tails and two polar head groups, in this case, they are not effective, due to their scarce solubility in water; this is also confirmed by the lower values of HLB.

Additives and stability of coating

Although used in very small quantities, additives can have a huge impact on coatings’ performance and application properties. The most difficult task is to find how to use them in the right order, at the right time, and at the right levels; additives can help improve the appearance and durability of a coating, the flow of paints and the efficiency of the manufacturing process, and other properties. One of the most important groups of additives is that of catalytically active additives, which include paint drying agents; they are added to air-drying coating formulations to catalyse the oxidative cross-linking reactions. In our study, cobalt, calcium and zirconium driers were tested singularly for each emulsion, and the only efficient drier was cobalt salt. Cobalt is a highly effective drier and a strong oxidant. It is usually added at 0.05 to 0.4%, depending on the binders’ concentration. At this stage of the experiments, once the suitable surfactants were found, several coatings were prepared to investigate the necessary concentration of cobalt, their drying rate at room temperature, and at which stage cobalt should be added to the coating. The results of drying rate are listed in Table 2. In all cases, coatings dried, and the formation of a film was observed. For EML01 A, EML02 B, cobalt was added at the end, after the emulsification of binders, and then sonicated again to disperse it; the concentration was 0.20%. With this procedure, the cobalt dispersed in the coating, although a longer time of sonication was required, but the emulsion was not stable, and eventual separation of phases occurred in the next days, with oxidation of binders. For the coatings EML03 C, EML04 D, EML05 E and EML06 F, the sequence was changed: cobalt was added to linseed oil and alkyd, before emulsification with water and surfactants. These coatings were more homogeneous; the dispersion was better and more stable.

Table 2.

Measurement of mass changes during the coating’s drying at room temperature

| EMULSION | Co (%) | Binder (%) | m (g) | m after 24h (g) | m after 48h (g) |
|----------|--------|------------|-------|----------------|----------------|
| EML01 A  | 0.20   | 22.7       | 2.00  | 0.51           | 0.50           |
| EML02 B  | 0.20   | 22.7       | 2.00  | 0.62           | 0.54           |
| EML03 C  | 0.10   | 17.3       | 2.04  | 0.48           | 0.41           |
| EML04 D  | 0.17   | 21.3       | 2.00  | 0.41           | 0.38           |
| EML05 E  | 0.11   | 20.9       | 2.00  | 0.48           | 0.40           |
| EML06 F  | 0.13   | 21.0       | 2.00  | 0.39           | 0.38           |
To prevent the formation of a film on top of the coating during storage, an anti-skinning agent was added to the formulation, specifically it is methyl ethyl ketoxime, which by binding of the drying agent, inhibits the oxidative crosslinking reactions of resin and drying oil before its utilization. During the emulsification, the formation of foam at the surface was observed with ethoxylated alcohols; this is an undesired property in the preparation process, and to avoid it, a silicone based antifoam agent was used. It turned out to be very efficient at very low concentrations. This antifoam agent can be added at any stage of the process.

Evaluation of coating penetration

The application of coatings on hydrothermally treated and untreated aspen wood samples resulted in different behaviours. The type of the substrate influenced the wetting properties of the coating and the absorption. A deeper penetration of the coating was observed for hydrothermally treated wood than for untreated wood. For hydrothermally treated wood, the coating penetrated from 5 to 15 mm, whilst for the untreated wood, it penetrated from 1 to 4 mm. This can be explained by the changes in the chemico-physical properties that occur after hydrothermal treatment: wood becomes more hydrophobic, has lower moisture content and its density decreases, making it more porous. This facilitates the absorption of the coating under the surface. Ulterior investigations are necessary to examine the distribution of binders at the wood-coating interface.

Conclusion

Our experiments confirmed that ethoxylated alcohol surfactants are effective dispersing agents in water-borne coatings. They provide a stable emulsion, dispersing alkyd and linseed oil without the disruption of droplets or coalescence. The use of ultrasonication to homogenize alkyd and linseed oil in water led to the formation of a white emulsion. In our experiments, only water was used as a solvent, avoiding the utilization of an organic cosolvent, which is usually present also in water-borne coatings. Cobalt proved to be a highly efficient drier, also at a low concentration, but there are some problems related to the dispersion and stability of the coating, and the sequence of the mixing order, eventually calcium and zirconium can be used together with cobalt drier, but not alone, since they showed a poor efficiency. Additional additives and a combination of surfactants should be further investigated to improve the coating stability. Due to chemico-physical changes of wood, in hydrothermally treated wood absorption and penetration of the coating is deeper than in untreated wood.

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