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Sundere Grundere
Alternatives to alkyphenol ethoxylates

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Sundere Grundere – alternatives to alkylphenol ethoxylates

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Foreword

The project 'Sundere Grundere – alternatives to alkyphenol ethoxylates' (APEO) was funded by the Danish Environmental Protection Agency's "Miljøeffektiv Teknologi 2013" and was carried out in the period from February 2014 to February 2016.

This report describes the project results and the methodology used to achieve the results. The purpose of the project was to substitute alkylphenol ethoxylates from two primer systems. The primer systems exhibit a sealing effect towards discolouration and odours from, e.g., fire-damaged materials, and this unique performance is hard to achieve when substituting the current binder system containing an APEO with alternative binders containing no APEOs. Alkylphenols and alkylphenol ethoxylates are on the List of Undesired Substances (LOUS) created by the Danish Environmental Protection Agency (the Danish EPA) as they are considered to be endocrine disruptors, toxic to reproduction and persistent in the environment. Denmark has a strategy for phasing out the use of AP and APEO.

The project was carried out by Danish Technological Institute (DTI) and was headed by MSc, PMP Gitte Tang Kristensen and PhD Helle Svendsen as project managers, with significant contributions from PhD Jacob Ask Hansen and PhD Helene Bendstrup Klinke from Danish Technological Institute, and Thomas Sørensen and Peter Dahl from Beck & Jørgensen A/S.

An advisory group followed the progress and results of the project, and the members of the advisory group were:

- Gitte Tang Kristensen, DTI
- Thomas Sørensen, Beck & Jørgensen A/S
- Sidsel Dyekjær, the Danish EPA

Conclusion and Summary

The current project concerns the substitution of alkylphenol ethoxylate (APEO) compounds in paint primer products. The APEO compounds are substances of concern due to negative effects on health and environment. APEOs are used in, e.g., paint products, and in the primers, which are the topic of this report, the APEOs are part of the binders and provide a blocking effect to avoid discoloration and emission of volatile organic compounds from wood and fire-damaged wood.

Through this project, alternative binders free of APEOs have been identified and they may substitute the binders used in two different primer systems: an industrial primer system with the APEO-containing binder Binder 1 and a sealing primer with the APEO-containing binder Binder 2.

Main results

The work carried out in this project has resulted in the identification of an alternative binder for the sealing primer. The new sealing primer is based on the binder Binder 15, which is free of APEO, and, to adjust stability, the emulsifier Emulsifier 1 has been added to the formulation. This has significantly improved the health and safety assessment of the primer, and the contents would allow the product to carry the EU Ecolabel. To obtain a sealing effect comparative to the existing primer, three layers of the alternative sealing primer should be applied instead of two, which were required for the sealing primer with Binder 2. The sealing primer formulation will be introduced to pilot production in continuation of the project.

For the industrial primer, the alternative binder Binder 3 looks promising to avoid APEO with regard to technical performance as well as a safe health and environmental profile; however, complete testing and formulation development has not been accomplished in the project period. The development work with Binder 3 will be continued after finalisation of the current project. Due to an urgent need for an alternative binder, a temporary binder system consisting of the binder Binder 7 and the additive Stainblocking additive 1 has been incorporated in an optimised formulation for the industrial primer, which is ready for pilot scale production. The alternative binder does not fulfil the technical requirements, which is the reason for including the additive. However; the additive compromises the health and environmental profile of the industrial primer due to the CLP classification as corrosive for skin and metal (Skin Corr. 1A H314 and Met Corr 1, H290). For these reasons, this is a temporary substitute to Binder 1, while the development work is continued to improve the primer product with Binder 3.

Summary of the work

In an identification phase, alternatives were sought mainly by screening and approaching suppliers broadly, which resulted in a set of six possible alternatives for the industrial primer and 10 possible alternatives for the sealing primer. The possible alternatives needed to comply with a set of technical requirements as well as a list of requirements concerning health and environmental effects of the alternative:

- Binders free of APEO.
- Binders free of substances of concern (like PBT/vPvB and SVHC, see chapter 6).
- Binders that can be formulated to sandable primers with similar or better tannin-blocking properties on wood than the current standard, without the use of zinc oxide or other reactive pigments or additives.

Besides the explicitly described technical requirements, a health and environmental assessment was carried out for each alternative (including other ingredients that differ from the original recipe) that had passed an introductory screening test. This screening implied a laboratory screening to evaluate all alternatives based on their basic property as a stain blocker, which included the ability to block colour breakthrough from ball pens, a red marker, nicotine and coffee.

The screening procedure reduced the possible alternatives for the sealing primer to just one binder: Binder 15, which showed superior stain-blocking properties. Then, the stability of the sealing primer formulation with Binder 15 was evaluated and revealed the need to add a stabilising emulsifier, which was included in the recipe. The recipe passed the following tests to a satisfactory level:

- Sensory evaluation of films applied to heat-treated wood: The sensory evaluation displays a slight tendency towards the odour of the sealing primer with Binder 15 and the emulsifier being less acceptable and more intense compared with the sealing primer with Binder 2.
- Emission of volatile organic compounds (VOCs) from films applied to heat-treated wood: Using three film layers of the sealing primer with Binder 15 and emulsifier resulted in the same retention of VOCs as for two layers of the sealing primer with the APEO-containing Binder 2.

Overall, the sealing primer with Binder 15 and emulsifier has been evaluated as a viable alternative to the sealing primer with Binder 2 with regard to technical performance, though three film layers are required instead of two. In addition, the health and environmental assessment is superior for the new formulation, as the binder does not contain APEO or other CLP-classified components, and the new product will be introduced into the product range.

Concerning the industrial primer, the screening test only slightly reduced the number of alternatives to Binder 1, meaning that tannin-blocking tests for four alternatives were carried out. In this test, the two alternative binders Binder 3 and Binder 5 performed well by blocking the tannins better from bleeding through the primer than the reference industrial primer. The samples were further studied to evaluate their mechanisms for hindering colour breakthrough. This revealed a stain-blocking mechanism for the industrial primer with the alternative binder Binder 3 and the alternative binder Binder 5, where no colouration of the primer closest to the wood surface took place, whereas the reference industrial primer with Binder 1 displayed a stain-locking mechanism, where the colouration was trapped in the primer layer. In addition, it was found that the colour breakthrough in the primer studies often occurred on sites with very thin coating layers, meaning that they were sensitive to anything that may cause film defects.

The alternative binders for the industrial primer were not fully technically evaluated in the project period, though the binder Binder 3 seemed superior with regard to both technical performance (colour or tanning blocking) and health and environmental effects. For this reason, optimisation and evaluation of this alternative for the industrial primer will continue after project finalisation. However, the need for a substitution for the industrial primer containing Binder 1 in order to avoid the use of APEO compounds is urgent. For this reason, the alternative binder Binder 7 was included in the ongoing testing and evaluations despite the fact that an additive with undesirable health and environment characteristics (contains CLP-classified components) had to be added to fulfil the stain-blocking properties. This provided a temporary substitute for the industrial primer with Binder 1, where the substitute has a better health and environmental profile than the current product, evaluated internally according to the criteria in Beck & Jørgensen's quality system This will allow Beck & Jørgensen to offer the product to customers continuously rather than having to stop selling the product until a better alternative is fully developed.

Konklusion og sammenfatning

Projektet omhandler substitution af alkylphenolethoxylater (APEO) i forseglende malingsgrundere. APEO-forbindelserne er problematiske stoffer pga. deres negative miljø- og sundhedseffekter. De anvendes i bl.a. malingsprodukter og i grundere, som er emnet for denne rapport, hvor de indgår som en komponent i binderne og bidrager med en forseglende effekt, som hindrer gennemtrængning af farve og flygtige organiske stoffer (VOC-forbindelser) fra bl.a. træ og brandskadet træ.

I dette projekt er der identificeret alternative bindere, som ikke indeholder APEO-forbindelser og som kan erstatte binderne anvendt i to forskellige grundersystemer: En industriel grunder med binderen Binder 1 og en forseglende grunder med binderen Binder 2. Begge disse indeholder APEO.

Hovedresultater

Det udførte arbejde i dette projekt har resulteret i identifikation af en alternativ binder til den forseglende grunder. Det nye grundersystem er baseret på binderen Binder 15, som ikke indeholder APEO, og grundersystemet er derudover tilsat emulgatoren Emulsifier 1 for at optimere produktets stabilitet. Denne substitution har forbedret miljø- og sundhedsvurderingen af produktet væsentligt, og indholdet i den nye grunder gør mærkning med EU's miljømærke Blomsten mulig. For at opnå en forseglingsevne, der svarer til den eksisterende grunder med Binder 2, kræves tre lag af den nye grunder mod det eksisterende systems to lag. Det nye grundersystem med Binder 15 overføres til pilotproduktion i fortsættelse af projektet.

Den alternative binder Binder 3 uden APEO viser lovende resultater til brug i den industrielle grunder, både mht. tekniske parametre og en klart forbedret miljø- og sundhedsprofil. Det har dog inden for projektperioden ikke været muligt at opnå en tilfredsstillende formulering til endelig test, hvorfor udviklingsarbejdet fortsættes efter projektets afslutning. Da der dog er opstået et akut behov for et alternativ til den nuværende binder, er der parallelt arbejdet med at indarbejde binderen Binder 7 og additivet Stainblocking additive 1 i den industrielle grunder og optimere denne formulering, således at denne er klar til pilotproduktion. Denne substitution var relativt simpel, men udgør kun en midlertidig løsning, idet binderen i sig i selv har en tilfredsstillende miljø- og sundhedsprofil, men ikke yder tilstrækkelig forsegling. Additivet Stainblocking additive 1 er nødvendigt for at opnå tilstrækkelig forseglingsevnen. Selvom systemet er frit for APEO og opfylder de tekniske krav, så det dermed er bedre end den eksisterende industrielle grunder, kompromitterer additivet den ønskede miljø- og sundhedsprofil pga. CLP-klassifikationen som ætsende for hud og metal (Met. Corr. 1 H290 og Skin Corr. 1A H314). Der arbejdes derfor videre med udvikling af en formulering med Binder 3 efter afslutning af projektet.

Opsummering af arbejdet

Alternative bindere blev fundet i en identificeringsfase ved at screene markedet bredt og kontakte leverandører, hvorved der blev identificeret seks mulige alternativer til den industrielle grunder og 10 mulige alternativer til den forseglende grunder. De mulige alternative bindere skulle leve op til en række tekniske krav samt en række krav til deres miljø- og sundhedseffekter:

- Bindere uden APEO.
- Bindere uden problematiske stoffer (fx PBT-/vPvB-stoffer og SVHC-stoffer, se kapitel 6).

- Bindere som kan formuleres til slibbare grundere med tilsvarende eller bedre tannin-forseglende effekt på træ sammenlignet med eksisterende produkter – uden brug af zinkoxid eller andre reaktive pigmenter eller additiver.

Foruden de angivne tekniske krav blev en miljø- og sundhedsvurdering udført for hvert alternativ (inklusiv eventuelle andre komponenter tilsat ved substitutionen), som var udvalgt gennem den indledende screening. Denne indledende screening bestod i laboratorietests for at evaluere alle alternativer ud fra deres basale egenskab til at hindre gennemtrængning af farvestoffer, bl.a. fra kuglepenne, spritttusch, nikotin og kaffe. Screeningen reducerede antallet af mulige alternativer til den forseglende grunder til binderen Binder 15, som viste overlegen forseglende effekt. Derefter blev stabiliteten af forseglingsgrunderen med Binder 15 evalueret, hvilket viste et behov for yderligere stabilisering vha. en emulgator, som blev indarbejdet i formuleringen. Denne gennemgik med tilfredsstillende resultater følgende tests:

- Sensorisk evaluering af film malet på varmebehandlet træ: Den sensoriske evaluering viste en lille tendens til, at lugten af den forseglende grunder med Binder 15 og emulgator var mindre acceptabel og mere intens sammenlignet den forseglende grunder med Binder 2.
- Emission of flygtige organiske stoffer fra film malet på varmebehandlet træ: Ved at påføre tre lag film af den forseglende grunder med Binder 15 og emulgator opnåedes samme tilbageholdelse af flygtige organiske stoffer som for to lag af den forseglende grunder med Binder 2.

Overordnet set blev den forseglende grunder med Binder 15 og emulgator vurderet til at være et relevant alternativ til den forseglende grunder med Binder 2 baseret på den tekniske funktion, idet der dog skal påføres tre filmlag i stedet for to. Derudover er systemet miljø- og sundhedsmæssigt overlegent, idet det ikke indeholder APEO-forbindelser og ikke er klassificeret, og produktet vil blive introduceret i Beck & Jørgensens produktsortiment.

For den industrielle grunder resulterede screeningen kun i en lille reduktion i antallet af alternativer til Binder 1, hvorfor der blev udført test af den tannin-forseglende effekt på fire alternativer. Her viste film med alternativerne Binder 3 og Binder 5 en bedre effekt end den eksisterende industrielle grunder mod gennemtrængning af tanniner. Mekanismen for filmenes evne til at hindre farvegennemtrængning blev yderligere undersøgt. Dette afslørede en "stain-blocking"-mekanisme for den industrielle grunder med de alternative bindere Binder 3 og Binder 5, idet der ikke blev observeret misfarvning af det inderste af filmen, som var tættest på træoverfladen. Derimod udviste den eksisterende industrielle grunder med Binder 1 en "stain-locking"-mekanisme, hvor der var misfarvning af det inderste af filmen tæt ved træoverfladen, dvs. farven blev fanget i grunderlaget. Yderligere blev det fundet, at farvegennemtrængning ofte blev observeret ved uregelmæssigheder i træets overflade, som gav anledning til meget tynde filmlag.

De alternative bindere til den industrielle grunder blev teknisk ikke fuldstændigt evalueret i projektperioden, men binderen Binder 3 viser stort potentiale mht. både teknisk funktion (hindring af farve- og tanningennemtrængning) samt miljø- og sundhedsprofil (reduceret indhold af CLP-klassificerede komponenter). Derfor fortsættes optimering og evaluering af dette alternativ til den industrielle grunder efter projektets afslutning. Pga. et akut behov for et alternativ til Binder 1 blev den alternative binder Binder 7 inkluderet i tests og evaluering på trods af at denne binder kræver anvendelsen af et additiv med uønskede miljø- og sundhedseffekter (indeholder CLP-klassificerede ingredienser) for at kunne hindre farvegennemtrængning. Dette gav en midlertidig erstatning for Binder 1, hvor miljø- og sundhedsprofilen for den industrielle grunder med Binder 7 og additivet samlet set ud fra Beck & Jørgensens interne kriterier er vurderet bedre end for den industrielle grunder med Binder 1, som indeholder APEO. Dermed har Beck & Jørgensen mulighed for at beholde produktet på markedet frem for at tage det af markedet for at afvente færdigudvikling af den industrielle grunder med Binder 3.

1. Introduction

In the paint industry, a number of traditionally used substances have been recognised as substances of concern due to new knowledge about their health and environmental effects. For years, the industry has worked to reduce, e.g., volatile organic compound (VOC) levels, and the implementation of the REACH regulation supports the trend towards products with a safer and more environmentally friendly profile.

The group of alkylphenols (APs) and alkylphenol ethoxylates (APEOs) is in the group of substances of concern, and the group is on the List of Undesirable Substances (LOUS) created by the Danish EPA. Major applications of APs/APEOs are in paint and lacquer, and nonylphenol ethoxylate (NPEO) is the most used APEO. Approx. 12% of the NPEO consumed is used in the paint industry (Lassen et al. 2013).

Through the last decade, paint producer Beck & Jørgensen A/S has worked to phase-out the use of APs and APEOs from their products, and, therefore, only a small fraction of their current product range contains APs and APEOs. The specific APEOs of concern in this project are NPEOs. They degrade to nonylphenols, which are considered endocrine disruptors and are classified as toxic to reproduction and toxic to the environment. NPEOs are non-ionic surfactants used as emulsifiers, wetting agents, dispersants, foam control agents and surface tension agents to, e.g., increase surface activity and improve the mixing of liquids (Lassen et al. 2013). The current project focuses on the substitution/removal of APEO compounds from two primer systems:

- A traditional industrial primer system that contains less than 1% of nonylphenol ethoxylate phosphate (NPEOP) in the binder.
- A special sealing primer system. This system contains a relatively small (1.3-1.6%), but necessary, amount of NPEO in a PVDC binder. This sealing primer system is used for products that aim to (*i*) seal, e.g., fire- or water damaged along with nicotine-polluted walls, (*ii*) function as wet-room primer, (*iii*) function as wood sealant and (*iv*) function as knot sealing.

The main focus of the project will be to identify binder systems capable of fulfilling the requirements to the individual primer systems, i.e., primarily a sealing effect towards discolouration for the industrial primer and combined sealing effects towards discolouration and odour breakthrough for the sealing primer.

2. Approach and methods

2.1 Approach taken to identify suitable alternatives

To identify suitable alternatives for the industrial primer and the sealing primer, a range of parameters have been evaluated; from availability through physical behaviour to health and environmental assessments. For the initial selection of alternatives of interest to this study, a series of supplier interviews were carried out to establish the availability of alternatives that do not contain APEOs, and to gain knowledge of their basic composition and formulation requirements. For further selection and evaluation of alternatives, a funnel approach (as illustrated in Image 1) was followed.

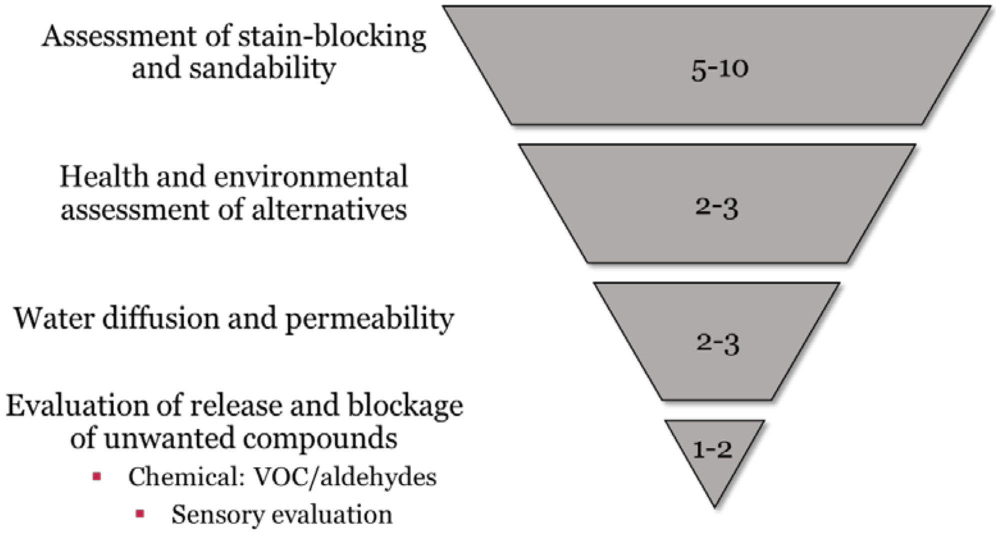

IMAGE 1
FUNNEL FOR SELECTION OF ALTERNATIVES. THIS APPROACH IS USED FOR BOTH INDUSTRIAL AND SEALING PRIMER.

This illustrates that the selected alternatives were assessed for their basic capabilities as a primer, such as stain- and tannin-blocking effects and knot-sealing effect along with physical properties such as sandability; which are all key elements of the needed performance and relatively easy to test. The binders that fulfil these requirements are then further evaluated in a health and environmental assessment. These steps were expected to reveal 2-3 alternatives that may be suitable for each primer system, and the alternatives were integrated into a primer formulation, i.e., with stability and rheological capabilities as expected for a final primer product. This was performed to further evaluate water diffusion and permeability and, finally, the release and blockage of unwanted compounds.

2.2 Description of methods

A number of tests are carried out to assess the performance of the alternative binders in paint formulations and paint films. The procedure for each test is described in the following sections.

2.2.1 Stain-blocking test

To evaluate the visual blocking effect of a primer with a given binder, stain-blocking tests were carried out. On a cardboard, horizontal lines were drawn/painted with three different ball pens, a red marker, an aqueous suspension of cigarette stubs (nicotine) and coffee. Reference and test primers were applied in vertical lines, 2 x 120 µm thick film layers, followed by 3 x 240 µm ceiling paint. Each film layer was left to dry for 24 h before re-application. After 24 h, the sealing effect was visually evaluated using a scale, where 0 is no blocking and 5 is full blocking (no discolouration).

2.2.2 Tannin-blocking test

In order to evaluate the blocking effect of a primer against water-soluble tannins, the following tests were performed. Small samples of Merbau (*Intsia spp*) were coated by brush with two layers of the primer and one layer of an acrylic topcoat. The drying time between each coating was 24 h, and after the application of the topcoat, the samples were dried at room temperature for seven days. Then they were immersed in tap water and evaluated after one day, three days, seven days or until it was possible to see any bleeding. The samples were evaluated visually and compared to the reference product.

2.2.3 Study of the binders and their sealing effect

To study the binder chemistry and sealing effects as well as the function and properties of the films, physical and chemical analyses of the primer films were carried out:

- leaching properties of the primer films were studied by cross-section microscopy analyses to reveal information on the properties and function of stain-blocking/stain-locking of the different primer films,
- to determine the hydrophilic/hydrophobic properties of the primer films, contact angle measurements were conducted.

2.2.4 Stability testing of formulations

Stability testing of coating formulations was carried out by accelerated testing in an oven. 24 h after production, the samples were tested regarding viscosity and pH, and then 450 ml of the sample was placed in an oven at 40 °C and the rest of the sample was stored at room temperature. The samples were tested again after seven, 14 and 28 days. If the viscosity change was lower than +/- 20%, the product was considered to be stable.

Rheological analyses (stress sweep and frequency sweep) were carried out as accelerated stability analyses, and results were compared to the results of the stability testing in an oven.

For the stress sweep (amplitude sweep), approx. 15 mL sample was poured into the cup in the rheometer (Physica MC301, Anton Paar), and the stress sweep was carried out by using a bob in the cup. Stress was applied at 1 Hz from 0.01-10 Pa. From the linear viscoelastic region (LVR) of the obtained data, the critical stress was calculated, i.e., where the stress had dropped 10%.

For the frequency sweeps, approx. 15 mL sample was poured into the cup in the rheometer (Physica MC301, Anton Paar), and the frequency sweep was carried out by using a bob in the cup. The stress used in the frequency sweeps was a stress below the critical stress divided by two to ensure that the frequency measurements were carried out within LVR. The frequency sweeps have been measured from 0.1-20 Hz at 1 Pa.

2.2.5 Sensory evaluation

The sensory evaluation was carried out according to the Danish Society of Indoor Climate: "Standard Test Method for Determination of the Indoor-Relevant Time-value by Chemical Analysis and Sensory Evaluation", 3rd ed. 2005.

Heat-treated wood (HTW) was prepared at Danish Technological Institute: Scots pine WTT process at 180 °C, 3 hrs hold. The sealant was applied according to the assignor's directions at 8 L/m^2 in one application by brush.

For sensory evaluation of the reference sealing primer, three types of test specimens were prepared with a total surface area of 2.6 m^2, corresponding to a material load of 7 m^2 floor in a standard room of 17.4 m^3:

- HTW
- HTW with sealing primer (705) white
- Sealing primer (705) on glass

Climate chamber	Climpaq, 200 L and 700 L glass chamber
Temperature	23 °C ± 2 °C
Relative humidity	50 ± 5% RF
Air change	0.9 l/s
Air velocity	0.1 – 0.2 m/s
Material load	2.6 m^2

TABLE 1
TEST CHAMBER CONDITIONS FOR SENSORY EVALUATIONS.

Sensory evaluation was carried out after three, seven and 28 days of conditioning of the test specimens in the Climpaqs (see data for conditioning in Table 1). An untrained panel of minimum 20 persons evaluated the intensity and the acceptability (scale given in Image 2) of the air from the Climpaq.

The criteria for acceptance according to the Danish Indoor Climate Labelling Scheme is an acceptability higher than 0 (just acceptable) and an odour intensity lower than 2.0 (moderate odour) according to the scaling given in Image 2.

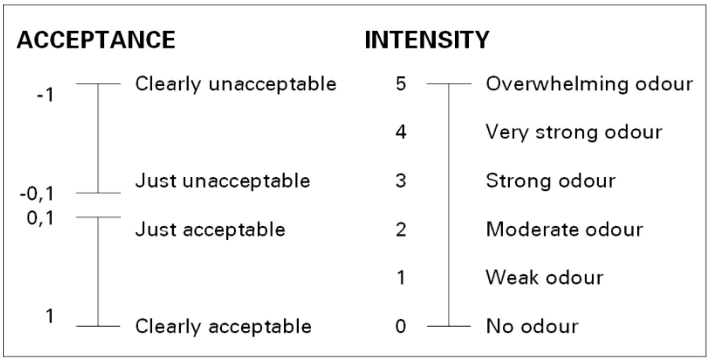

IMAGE 2
ACCEPTANCE CRITERIA ACCORDING TO DANISH INDOOR CLIMATE LABELLING SCHEME.

2.2.6 VOC determination

Sampling of air was performed with calibrated pumps from the Climpaq exhaust funnels and climate chambers for chemical analysis of volatile organic compounds (VOCs). Air sampled on Tenax sorbent tubes was analysed for VOCs by TDS-GC-MS according to ISO 16000-6. The concentrations were calculated with calibrated reference standards or as toluene equivalents with a lower reporting limit of 1 µg/m^3. Carbonyls including formaldehyde were collected on DNPH tubes and analysed by HPLC according to ISO 16000-3 with a quantification limit of 1 µg/m^3.

3. Identification of APEO alternatives

3.1 Identification of alternatives

The first step in the substitution process concerned the identification of alternatives to the specific APEOs. In this project, suppliers of binders were approached. Through an interview, the project partners requested alternative binders free of AP and APEO that may be suitable for the two primer systems: industrial primer and sealing primer, respectively. In this chapter, the alternatives for each system are described.

3.1.1 Industrial primer

The binder used in the current industrial primer offered by Beck & Jørgensen is an anionic, all acrylic copolymer emulsion (Binder 1) containing less than 1% NPEOP.

Alternatives for substituting Binder 1 were identified from interviews with leading suppliers of binders, and the alternatives are listed in Table 2. The preliminary criteria for alternative binders described to the suppliers were:

- binders free of APEO
- binders free of substances of possible concern (like PBT/vPvB and SVHC)
- binders that can be formulated to sandable primers with similar or better tannin-blocking properties on wood than the current standard, without the use of zinc oxide or other reactive pigments or additives.

Supplier	Name	Ref. no.	Type	Chemistry
Supplier 1	*Binder 1	1	Anionic	Acrylic polymer
Supplier 1	Binder 3	2	Cationic	Acrylic polymer
Supplier 1	Binder 4	3-1	Cationic	Acrylic polymer
Supplier 3	Binder 5	4	Anionic	Styrene acrylic copolymer
Supplier 4	Binder 6	5-1	Cationic	Acrylic polymer
Supplier 1	Binder 7	6	Anionic	Acrylic copolymer

TABLE 2
CURRENT BINDER SYSTEM (*BINDER 1) AND ITS ALTERNATIVES FOR THE INDUSTRIAL PRIMER.

The characteristics of the identified alternative binder systems vary; both anionic and cationic binders were represented, and the polymer types are in some cases different from the current binder Binder 1.

For most applications, an anionic binder/surfactant is preferred, since the cationic binders can cause agglomeration in the paint formulation, which is most often non- or anionic. This affects handling and use of the paint, and, for instance, residual paint may agglomerate and block paint sprayers etc. However, cationic systems may be applicable in some companies, where primer and topcoat are applied by using separate spray equipment and was, for this reason, included in the list of alternatives for further testing.

3.1.2 Sealing primer

The binder used in the current sealing primer offered by Beck & Jørgensen is a cationic polyvinylidene chloride (PVDC) polymer emulsion (Binder 2) containing 1.3-1.6% NPEO. NPEO is a surfactant added to the binder formulation to ensure a good compatibility of the binder with the rest of the paint formulation.

Initially, APEO-free alternatives were identified by supplier interviews, and the identified binder alternatives for the sealing primer are listed in Table 3. The binder criteria for sealing primer are different from binder criteria for the industrial primer since the main use of sealing primer is as a stain- and odour-blocking primer for interior use as well as wet room primer. Additional applications are as a knot sealer and as an end-grain sealer. However, preliminary criteria stated to suppliers included the need to avoid alternative binders with substances of possible concern (like PBT/vPvB and SVHC).

Supplier	Name	Ref. No.	Type	Chemistry
Supplier 1	*Binder 2	1	Cationic	PVDC
Supplier 2	Binder 8	2	Cationic	Alkyd emulsion
Supplier 2	Binder 9	3	Cationic	Alkyd emulsion
Supplier 3	Binder 10	4	Anionic	Acrylic polymer
Supplier 3	Binder 11	5	Anionic	Styrene acrylic copolymer
Supplier 3	Binder 12	6	Anionic	Acrylic copolymer
Supplier 3	Binder 13	7	Anionic	Acrylic copolymer
Supplier 5	Binder 14	8	Anionic	X-link acrylic copolymer
Supplier 6	Binder 15	9	Cationic	PVDC
Supplier 7	Binder 16	10	Cationic	Acrylic polymer

TABLE 3
CURRENT BINDER SYSTEM (*BINDER 2) AND ITS ALTERNATIVES FOR THE SEALING PRIMER.

Again, different polymer systems are used in the different binders identified. The alternative from Supplier 6 is a cationic PVDC system, as is the current binder system, Binder 2. From Supplier 2, two cationic alkyd emulsions were identified as potential candidates for testing, and Supplier 3 had supplied four emulsions: three anionic acrylic copolymers and an anionic styrene acrylic copolymer. As for the industrial primer system, Beck and Jørgensen prefers non- or anionic systems, as they provide fewer difficulties in the application equipment (spray guns, etc.).

4. Initial screening

4.1 Choice of screening methods

In order to screen the alternatives to the APEO-containing binders for both the industrial and sealing primer, a number of tests have been carried out. The industrial primer was required to visually seal against discoloration from underlying material/compounds breaking through the paint, whereas the sealing primer had several purposes as given in Table 4.

Primer system	Industrial primer	Sealing primer	Chapter
Basic requirement: Sealing property	Seal compounds that may cause discolouration from wood	Seal compounds that may cause discolouration. Seal VOCs from smoke-damaged surfaces (fire damage and/or smoke pollution). Seal moisture (in wet rooms). Seal smell.	-
Initial screening test	Stain-blocking test	Stain-blocking test	4
Extended screening	Tannin-blocking test Physico-chemical properties	Physico-chemical properties Sensory evaluation VOC determination	5
Separate evaluation	Environmental and health assessment of binder alternatives	Environmental and health assessment of binder alternatives	6

TABLE 4
SEALING PROPERTY REQUIREMENTS AND LISTING OF THE INITIAL AND EXTENDED SCREENING TESTS FOR THE PRIMER SYSTEMS.

In the same table, preliminary screening tests that allow many alternatives to be evaluated effectively are given for each system. The preliminary screening tests discard binders that do not fulfil the basic sealing requirements at an early stage. Stain-blocking tests were performed for all alternatives given for each primer system, which reduced the number of alternatives for the more comprehensive water diffusion tests.

In addition to these tests, the sealing effect for both chemical diffusion of VOCs and odour in general from HTW was evaluated in case of the sealing primer. As the human nose is very sensitive, it is typically not possible to evaluate the blocking of odours from chemical analyses alone, and the chemical analyses of HTW samples were supplemented by sensory analyses.

4.2 Primer recipe

The recipe used in the tests below was adjusted in order to use the same amount of binders to make them comparable. The reference primers were an industrial primer named 923 and a sealing primer named 705, and all primer recipes were based on this recipe, as given in Table 5. The binders varied according to the alternatives listed in Table 2 and Table 3 for industrial primer and sealing primer, respectively.

Substance	Amount (%)
Binder	80
Neutralizing agent	<1
Defoamer	<1
In-can preservative	<1
Film-forming solvent	-
Colorant	20
Thickening agent	<1

TABLE 5
FORMULATION OF PRIMERS.

4.3 Stain-blocking tests

The blocking effect of paint formulations towards visual breakthrough of certain compounds was evaluated on the basis of their performance in stain-blocking tests carried out as described in section 2.2.1.

4.3.1 Industrial primer

To the industrial primer system, visual blocking is of importance, whereas sealing of odour and VOCs is not required. The results from the stain-blocking test offered a guideline for choosing, which alternative binders to deselect and which to pass on for further testing.

The primer systems were analysed in stain-blocking tests, and results are documented in Image 3 and Table 6 with the evaluations outlined in Table 7. Due to a very poor stain-blocking performance of the alternative Binder 7, Beck & Jørgensen chose to test this binder including a tannin-stain inhibitor additive (Stainblocking additive 1). This solution was included despite an unsuitable health and environmental assessment of the additive, as this binder alternative would serve as an easy replacement for Binder 1 using the original recipe and due to an urgent need for an alternative during the progress of the project.

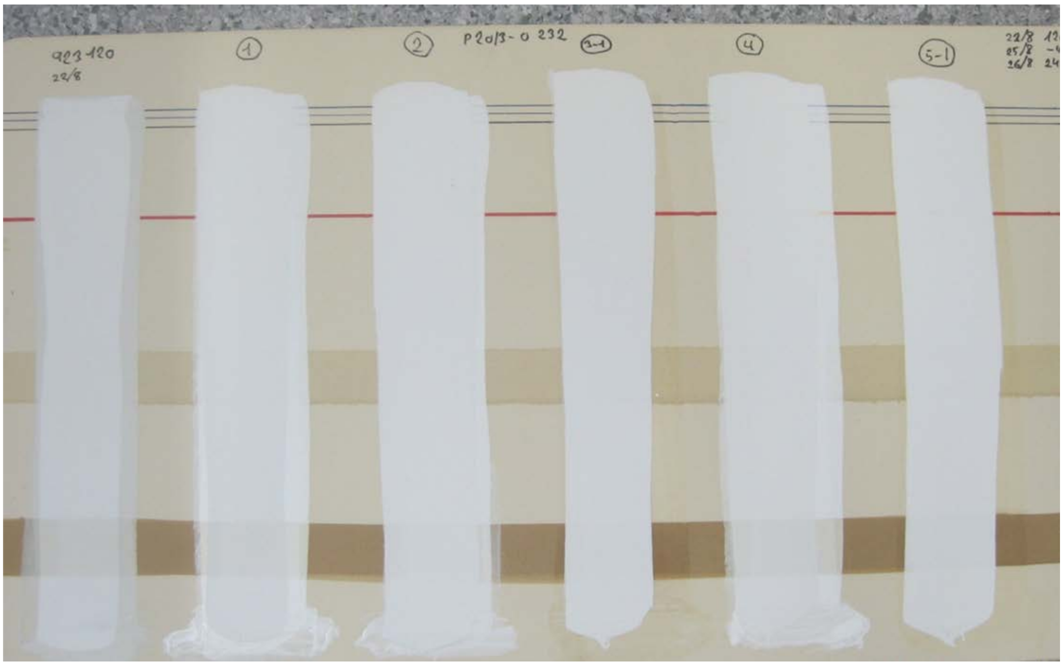

IMAGE 3
STAIN-BLOCKING TESTS WITH SELECTED BINDER SYSTEMS FOR THE INDUSTRIAL PRIMER. HORIZONTAL LINES ARE (STARTING FROM THE TOP): THREE DIFFERENT BALL PENS, A PERMANENT MARKER, NICOTINE AND COFFEE. VERTICAL WHITE LINES ARE PRIMERS WITH DIFFERENT BINDERS (STARTING FROM LEFT): REFERENCE SYSTEM 923, REF. NO. 1, 2, 3.1, 4 AND 5-1 (SEE TABLE 2 OR TABLE 6 FOR REFERENCE NUMBERS).

Ref. no.	Binder name	Ball pens	Red marker	Nicotine	Coffee
1	Binder 1	4	4.5	4	2
2	Binder 3	4	4.5	4	3.5
3-1	Binder 4	4.5	4.5	4	4
4	Binder 5	3.5	4	4	2
5-1	Binder 6	4.5	4.5	4	3.5
6	Binder 7 + Stainblocking additive 1	4	4	4	1
923	Binder 1	4	4	4	1

TABLE 6
DETAILED RESULTS FROM STAIN-BLOCKING TESTS OF INDUSTRIAL PRIMER WITH VARYING BINDERS.

By evaluating the stain-blocking results, the most promising candidates turned out to be the alternatives Binder 3, Binder 4 and Binder 6. Binder 7 plus Stainblocking additive 1 performed equally well as the reference system 923. Unfortunately, Binder 4 and Binder 6 could not be tinted with the colorant due to severe flocculation, leading to the need for further testing (tannin-blocking test, see section 5.1.1).

Ref. no.	Binder name	Notes/evaluation
1	Binder 1	Reference binder using test recipe
2	Binder 3	Good stain-blocking properties, but could cause problems due to the cationic nature of the binder
3-1	Binder 4	Good stain-blocking properties, despite tested as colourless due to flocculation of the tinting paste
4	Binder 5	Pinholes and low thickener response
5-1	Binder 6	Good stain-blocking properties despite tested as colourless due to flocculation of the tinting paste
6	Binder 7 + Stainblocking additive 1	Performs equally well as the reference 923 with Binder 1
923	Binder 1	Reference with Stainblocking additive 1

TABLE 7
SUMMARY OF OBSERVATIONS FROM STAIN-BLOCKING TESTS OF INDUSTRIAL PRIMER SYSTEMS BASED ON 923.

4.3.2 Sealing primer

Visual blocking to avoid discolouration is of importance to the sealing primer, and so is sealing against odour and VOCs. However, visual blocking was an essential and efficient screening tool to reduce the number of candidates for the next tests. Results are documented in Image 4 (ref. no. 1-7), Image 5 (ref. no. 8-10) and Table 8 (ref. no. 1-10), whereas evaluations are summarised in Table 9.

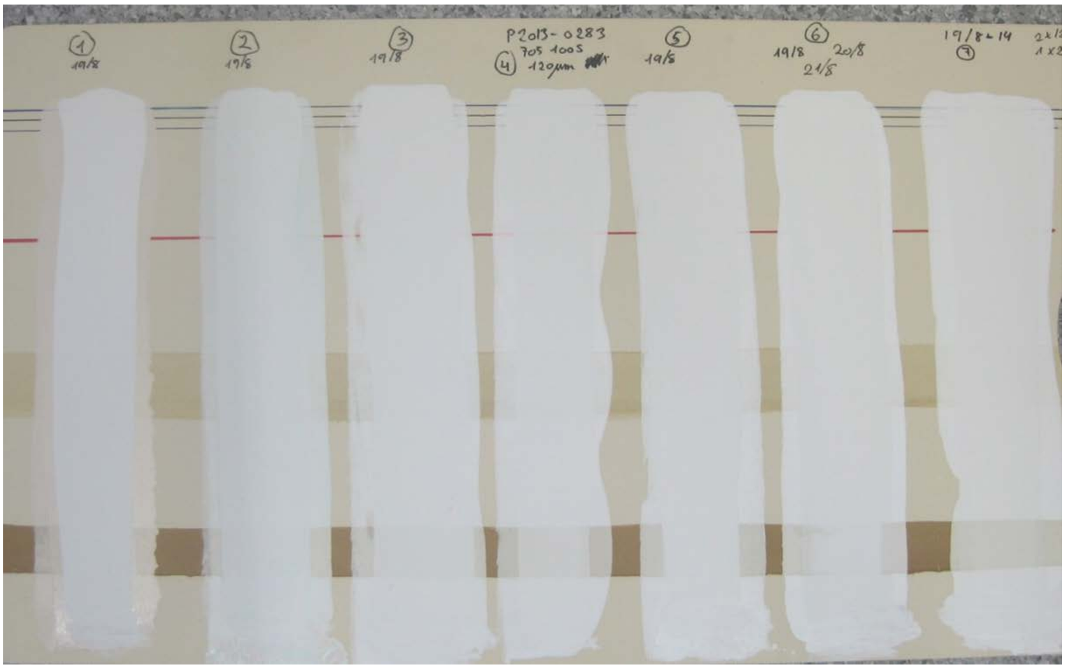

IMAGE 4
STAIN-BLOCKING TESTS WITH SELECTED BINDERS FOR THE SEALING PRIMER. HORIZONTAL LINES ARE (STARTING FROM THE TOP): THREE DIFFERENT BALL PENS, A PERMANENT MARKER, NICOTINE AND COFFEE. VERTICAL WHITE LINES ARE PRIMERS WITH DIFFERENT BINDERS (STARTING FROM LEFT): REF. NO. 1, 2, 3, 4, 5, 6 AND 7 (SEE TABLE 3 OR TABLE 8 FOR REFERENCE NUMBERS).

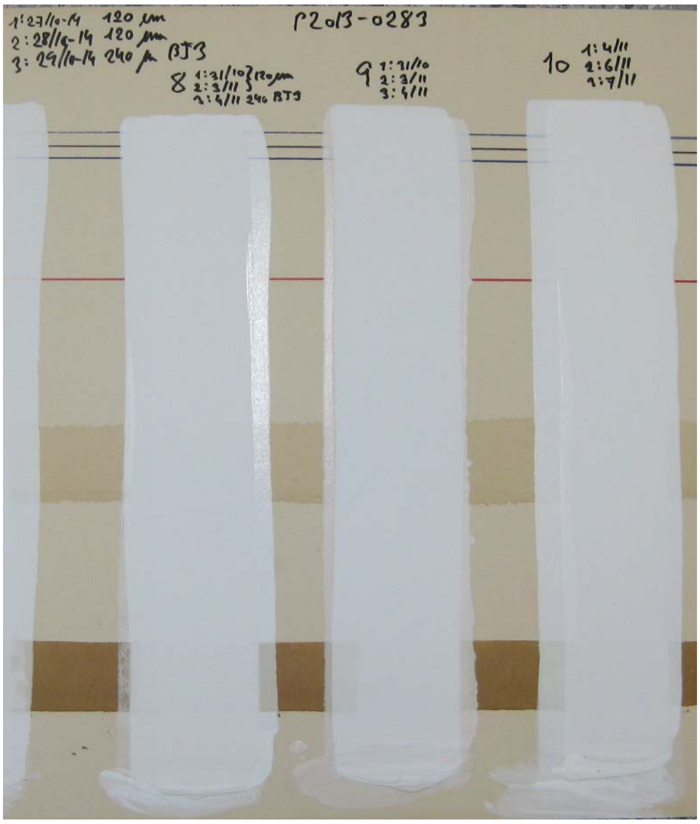

IMAGE 5
STAIN-BLOCKING TESTS WITH SELECTED BINDERS FOR THE SEALING PRIMER. HORIZONTAL LINES ARE (STARTING FROM THE TOP): THREE DIFFERENT BALL PENS, A PERMANENT MARKER, NICOTINE AND COFFEE. VERTICAL WHITE LINES ARE PRIMERS WITH DIFFERENT BINDERS (STARTING FROM LEFT): REF. NO. 8, 9 AND 10 (SEE TABLE 3 OR TABLE 8 FOR REFERENCE NUMBERS).

Ref. no.	Binder name	Ball pens	Red marker	Nicotine	Coffee
1	Binder 2	5	5	5	4.5
2	Binder 8	5	4.5	4	4
3	Binder 9	4.5	5	4	3
4	Binder 10	3.5	3.5	3.5	2
5	Binder 11	4.5	5	4	4.5
6	Binder 12	4.5	5	4	3
7	Binder 13	4	4	4	1
8	Binder 14	4,5	5	5	4.5
9	Binder 15	5	5	5	4,5
10	Binder 16	4.5	5	5	4

TABLE 8
DETAILED RESULTS FROM STAIN-BLOCKING TESTS OF SEALING PRIMER WITH VARYING BINDERS.

From the stain-blocking results, Binder 15 was identified as a suitable direct alternative to Binder 2, whereas Binder 11 sealed well, though the film turned pink or yellow when drying and was therefore not considered suitable for the sealing primer. However, it was in parallel with the rest of the project, tested for use in a sealing ceiling paint. Following these stain-blocking tests, the selected binders were subjected to further sealing tests (stability, chemical analyses and sensory tests/VOC emissions, see section 5.2).

Ref. no.	Binder name	Notes/evaluation
1	Binder 2	Reference binder using test recipe
2	Binder 8	Good stain-blocking properties
3	Binder 9	Good stain-blocking properties, except for coffee
4	Binder 10	Too much staining from coffee
5	Binder 11	Despite problems with foaming, the stain-blocking properties are good
6	Binder 12	Good stain-blocking properties, except for coffee
7	Binder 13	A lot of staining from coffee
8	Binder 14	Good stain-blocking properties
9	Binder 15	Performance similar to reference; however, turns pink after some time
10	Binder 16	Good stain-blocking properties

TABLE 9
SUMMARY OF OBSERVATIONS FROM STAIN-BLOCKING TESTS OF SEALING PRIMER.

5. Technical evaluation of alternatives

In the screenings in chapter 4, the stain-blocking properties significantly reduced the number of suitable binder alternatives for both primer systems. Therefore, the further evaluation was based on Binder 15 for the sealing primer, and, for the industrial primer, on Binder 3, Binder 4 and Binder 6. Due to the flocculation challenges with Binder 4 and Binder 6, Binder 5 was also included in the evaluation, whereas Binder 7 was included as a backup due to excellent performance when using the – though undesirable – additive to ensure stain-blocking.

In this chapter, the binder alternatives for the industrial primer are evaluated first, and then they are followed by the evaluation of the binder alternative for the sealing primer. Some studies are common for both systems and will therefore occur twice (once for each set of binders). Others will only occur once for the relevant primer system.

5.1 Evaluation of industrial primer

5.1.1 Tannin-blocking test of industrial primer

The formulation samples previously exposed to the stain-blocking test on cardboard were also tested on Merbau (*Intsia spp*) to evaluate their tannin-blocking proporties. All primers were prepared as the 923 with the respective alternative binders except for Binder 5, which was prepared in an alternative primer formulation (RV 571) recommended by the supplier for this specific system. The primer systems were applied and tested according to the method described in 2.2.2, and the results were compared to the results obtained for the reference product 923 with Binder 1 after 0, 21 and 56 days (see Image 6 to Image 9).

Reference 923

Binder 3

0 days | 21 days | 56 days

IMAGE 6
RESULTS OF TANNIN-BLOCKING TEST OF BINDER 3.

After 21 days, the reference became stained and after 56 days, the staining was very clear. Binder 3 showed no stains after 21 days, but after 56 days, stains were visible; though, not as distinct as on the reference (Image 6).

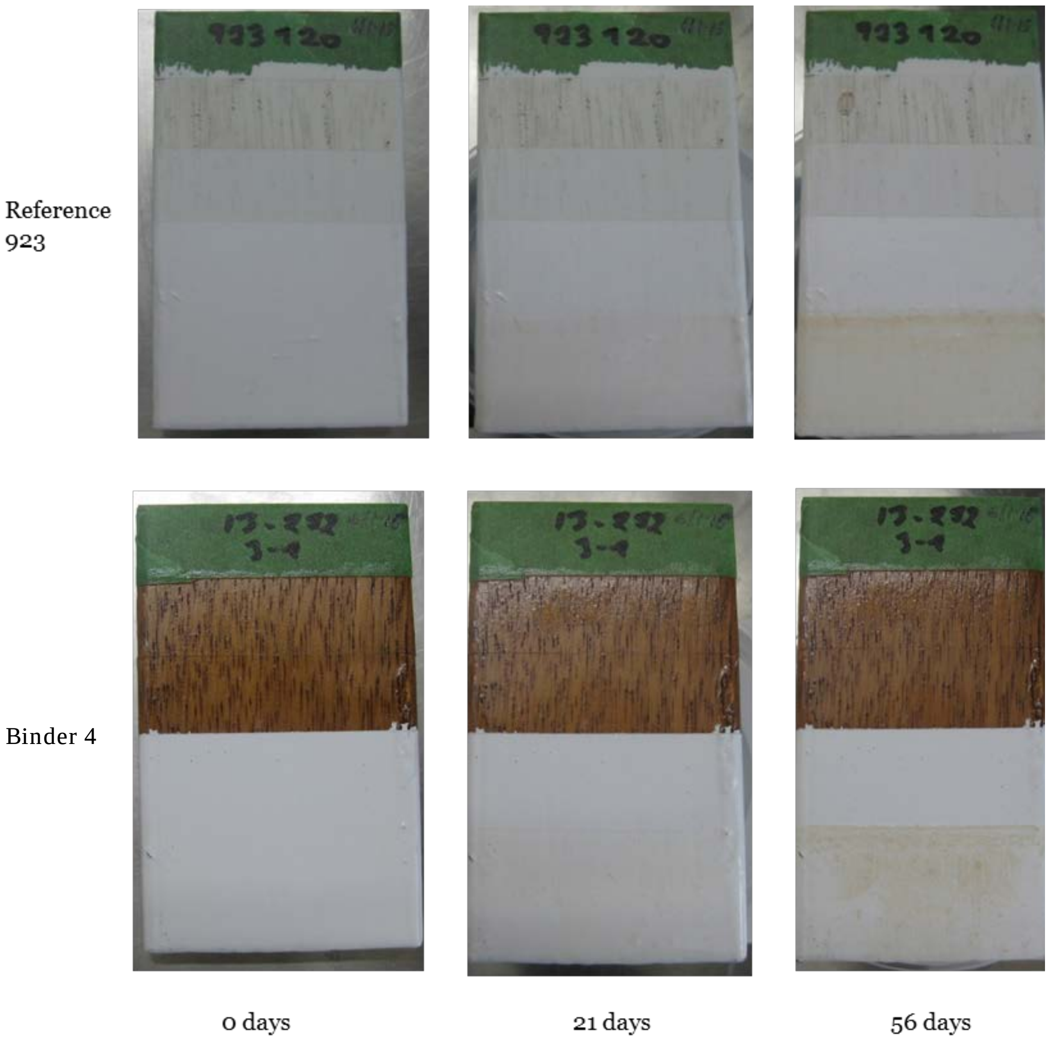

IMAGE 7
RESULTS OF TANNIN-BLOCKING TEST OF BINDER 4.

After 21 days, the reference became stained and after 56 days, the staining was very clear. Binder 4 showed no stains after 21 days, but after 56 days, stains were visible; though, not as distinct as on the reference (Image 7).

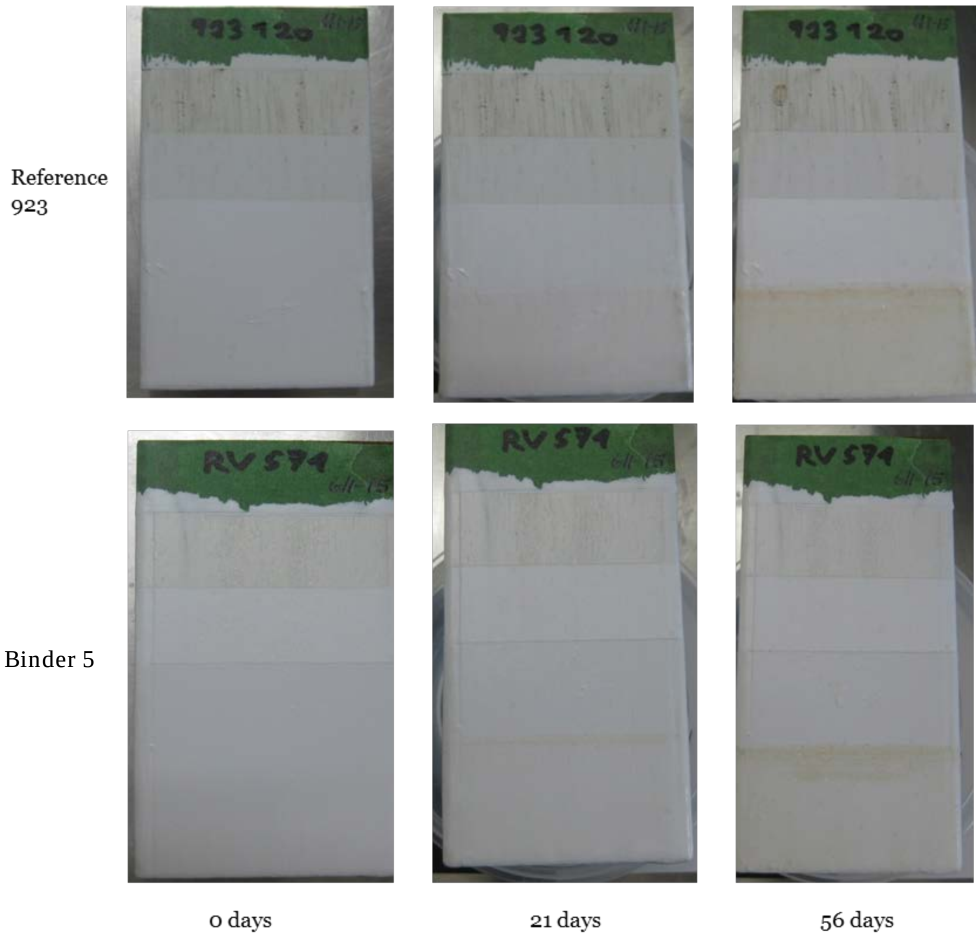

IMAGE 8
RESULTS OF TANNIN-BLOCKING TEST OF BINDER 5.

After 21 days, the reference became stained and after 56 days, the stain is very claear. Binder 5 showed no stains after 21 days, but after 56 days, stains were visible; though, not as distinct as on the reference (Image 8).

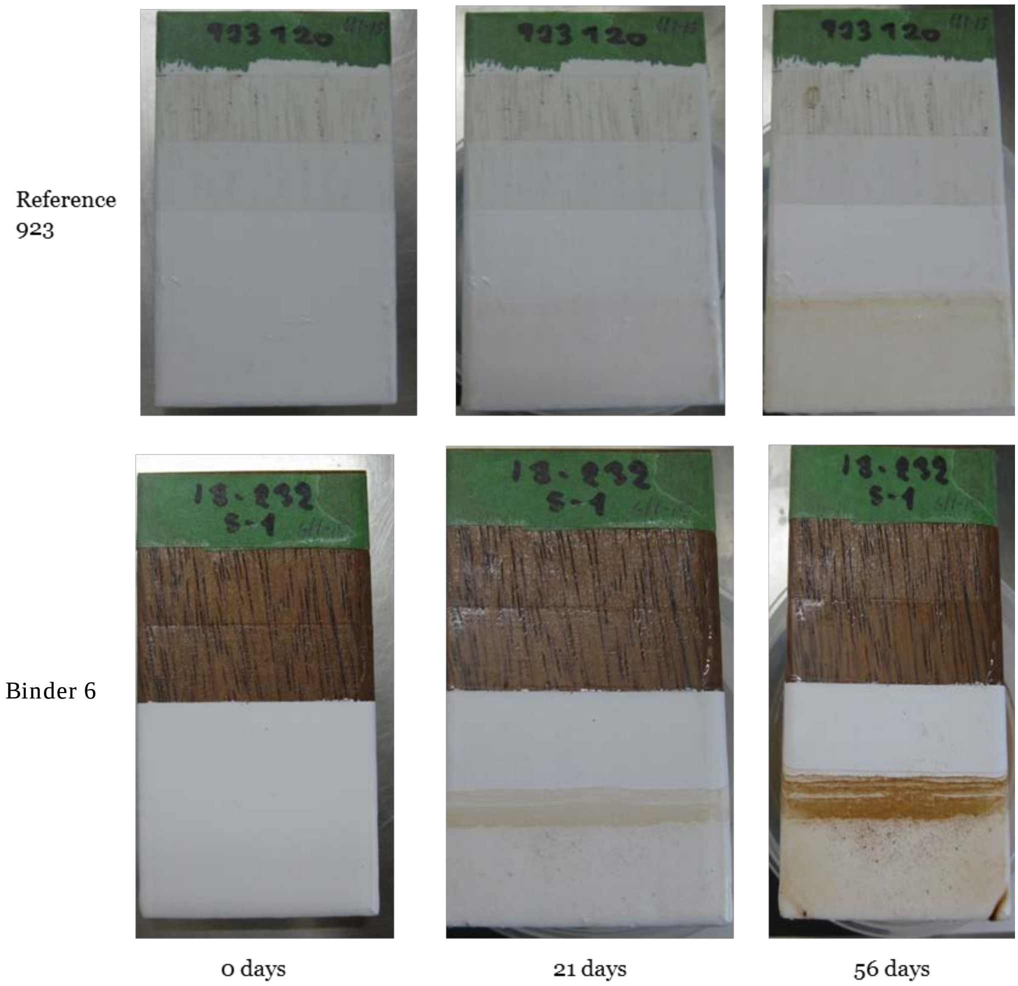

IMAGE 9
RESULTS OF TANNIN-BLOCKING TEST OF BINDER 6.

After 21 days, the reference became stained and after 56 days, the staining was very clear. Binder 6 showed distinct stains after 21 days, and after 56 days, more staining was evident and even more evident than on the reference (Image 9).

On the basis of the tannin-blocking results, Binder 3 and Binder 5 (in formulation RV 571) seemed to be the best performing products, and they were slightly better when compared to the reference primer 923.

5.1.2 Study of the binders and their sealing effect

A microscopy analysis of cross sections of applied film layers for tannin-blocking tests was expected to reveal information on the stain-blocking mechanisms of the different alternatives. Light microscopy analysis of cross sections of the reference system 923 with Binder 1 was used to validate this. An example of the images obtained is given in Image 10 below. In this image, the layers of paint from the spray application are apparent, and the total film thickness was evaluated to be app. 60 μm. No evidence of bubbles from foam was identified in this reference film.

IMAGE 10
CROSS-SECTION MICROSCOPY IMAGE OF A CROSS-SECTION OF THE REFERENCE SYSTEM 923.

The selected binder alternatives were studied for blocking/locking properties via cross-section microscopy. The primer samples used in tannin-blocking tests were studied to elucidate whether the films with alternative binders lock or block the discolouring compounds from breaking through.

These cross-section images are illustrated in Image 11 below, where the reference industrial primer with Binder 1 is compared to 923 with Binder 3, 923 with Binder 5 and, as an extra reference, 705 with Binder 2. As stated in 2.2.2, these samples were prepared with two layers of primer and one layer of an acrylic topcoat.

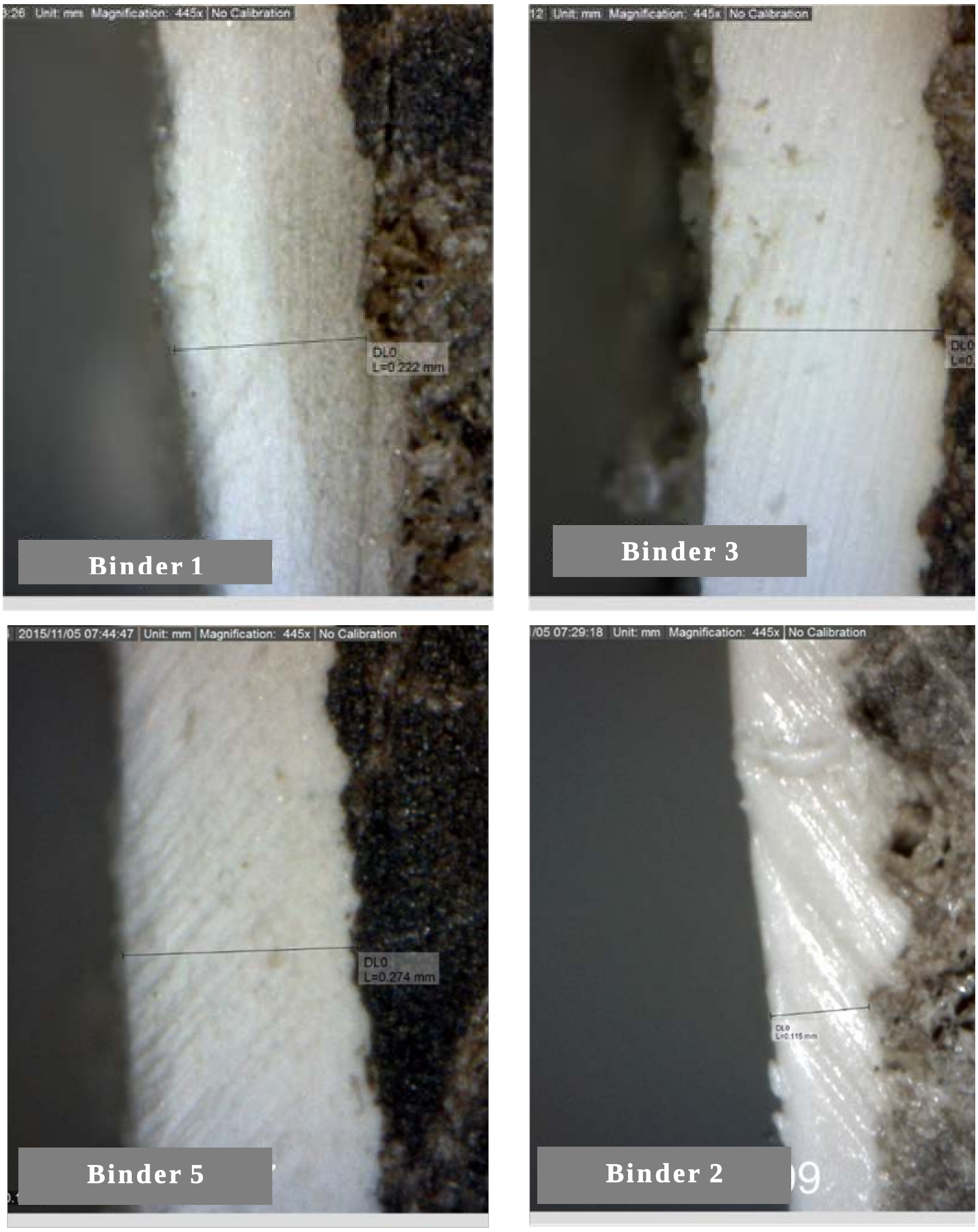

IMAGE 11
CROSS-SECTION MICROSCOPY IMAGE OF A THE INDUSTRIAL PRIMER SAMPLES AFTER THE TANNIN-BLOCKING TESTS. BINDER 2 IS INCLUDED AS AN ALTERNATIVE REFERENCE FOR A PRIMER SYSTEM.

From these cross-section images, it was evident that there are different modes of operation for the reference 923 with Binder 1 system and the primers 923 with alternatives Binder 3 and Binder 5. Here, in 923 with Binder 1 a colouration of the coating layers near the wood surface was observed, indicating a stain-locking mechanism, where the colouration was trapped in the primer layer. However, for primers 923 with the alternatives Binder 3 and Binder 5 the analyses indicated stain-blocking, as there was no evident “stain-front” in the coating layer, i.e., it was blocked by the primer. The same was evident for primer 705 with Binder 2. Furthermore, studies of colour breakthrough in the primers with alternative binders indicated that these are highly dependent on the thickness of the primer, and colour breakthrough was often observed at defects in the wood surface, where breakthrough was caused by a very thin layer of coating at the specific site of breakthrough. The defect at a spot with colour breakthrough is shown in Image 12 below.

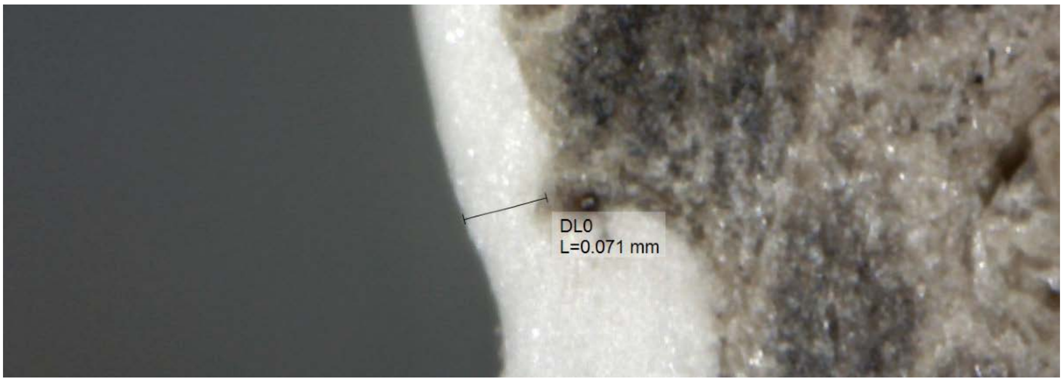

IMAGE 12
EXAMPLE OF SURFACE DEFECT SEEN IN CROSS-SECTION MICROSCOPY IMAGE OF AN INDUSTRIAL PRIMER SAMPLE AFTER THE TANNIN-BLOCKING TESTS. COLOR BREAKTHROUGH WAS OBSERVED MAINLY AT THESE DEFECTS.

To study the correlation between permeability and primer hydrophilicity, water contact angles on the pure primers and reference recipes were measured. Examples of droplet forms are given in Image 13 below.

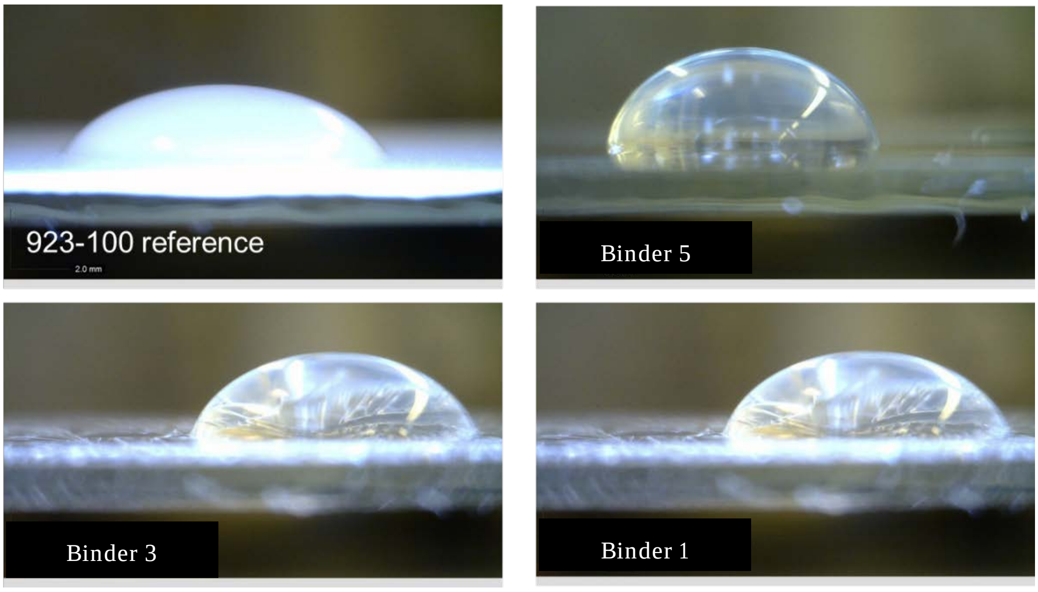

IMAGE 13
DROPLET FORMS FROM WATER CONTACT ANGLES FOR THE PURE PRIMERS AND THE 923-100 REFERENCE RECIPE CONTAINING BINDER 1.

Table 10 below shows the measured contact angles for films of the two binder alternatives compared with the current binder Binder 1. Only little difference between the binder films was observed; the contact angles of the two alternatives were slighty higher than for the reference binder Binder 1, indicating a slight decrease in the hydrophilic properties going from the Binder 1 binder to Binder 3 to Binder 5. It was also noted that the final 923 formulation resulted in a higher degree of hydrophilicity compared to the neat primers. These small changes in water contact angles from Binder 1 to Binder 3 to Binder 5 were not expected to have a major impact on the water-blocking properties of the final primer mixture. Here, the difference obtained when mixing the binder into the primer recipe was expected to have a larger impact on the overall hydrophilicity of the film surface.

Sample	Water contact angle
Binder 1	71°
Binder 3	76°
Binder 5	81°
923-100 reference	57°

TABLE 10
WATER CONTACT ANGLES DETERMINED FOR BINDER FILMS FOR THE INDUSTRIAL PRIMER SYSTEM.

5.2 Evaluation of sealing primer

5.2.1 Film surface studies

For the sealing primer, contact angle measurements of films of the current binder Binder 2 and the alternative Binder 15 were conducted to evaluate the hydrophobicity/hydrophilicity of the two film samples. As given in Table 11 below, the contact angles of the pure binders were very comparable and much more hydrophilic than binders in the industrial sealer systems. Therefore, the final primer was expected to have a similar hydrophilic behaviour for Binder 2 and Binder 15, respectively.

Binder	Water contact angle
Binder 15	31°
Reference, Binder 2	31°

TABLE 11
WATER CONTACT ANGLES DETERMINED FOR BINDER FILMS FOR THE SEALING PRIMER SYSTEM.

5.2.2 Stability testing

Stability testing of formulations was carried out by simple storage at room temperature, accelerated testing in ovens and by rheological analyses.

At room temperature, the reference 705 with Binder 2 seemed unstable, whereas it seemed stable when kept at 40 °C. For 705 with Binder 15 the opposite seemed to be the case, as the sample at room temperature seemed stable, whereas it coagulated when stored at 40 °C.

In a stress and frequency sweep, the elastic modulus, G', and the viscous modulus, G'', were measured as a function of stress or frequency, indicating the elastic and viscous contributions. In order to analyse the results, tan δ was used. Tan δ is given by the ratio between the viscous and the elastic contribution, G''/G'; therefore, a low tan δ indicates an elastic material, whereas a higher tan δ indicates a more viscous, less structured material (Mezger 2002; Whittingstall). In other words, a more elastic material is more stable compared to a viscous, less structured material.

Stress sweep (amplitude sweep)

From the stress sweep measurement shown in Image 14 it was observed that G' is higher than G'', indicating gel character of both samples.

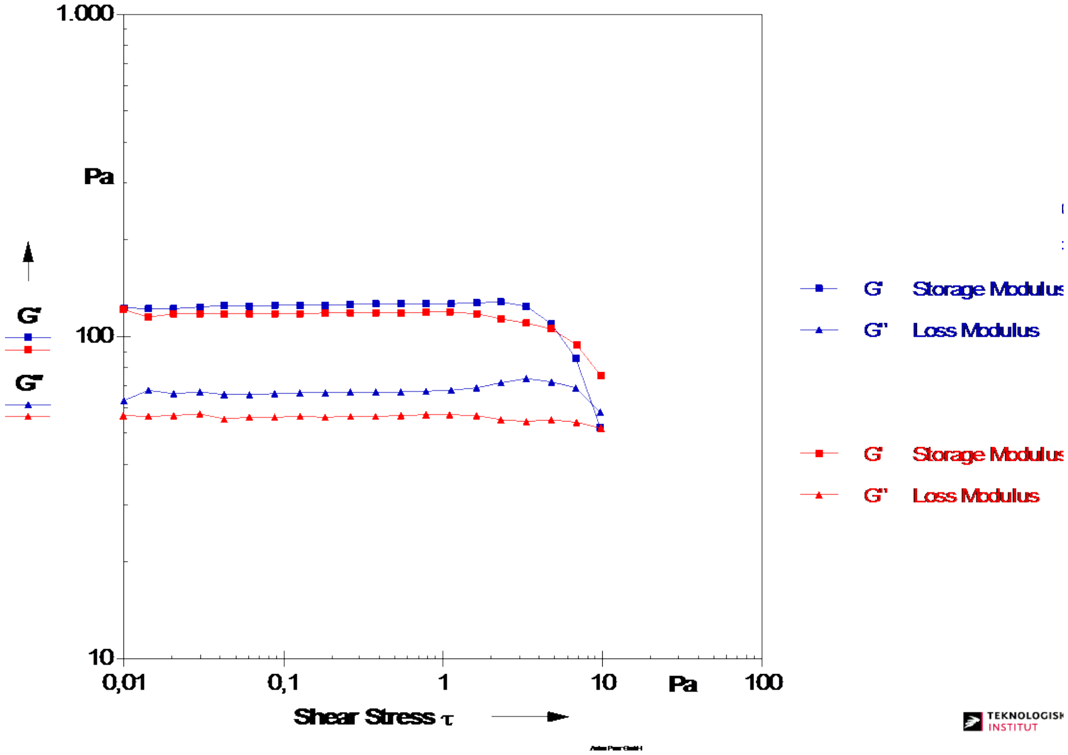

IMAGE 14
STRESS SWEEPS OF REFERENCE 705 WITH BINDER 2 (BLUE) AND 705 WITH BINDER 15 (RED).

G' is used to determine the length of the linear viscoelastic region (LVR), which indicates the stability of a sample. The critical stress is used as a measure for the length of this area. A short LVR (low critical stress) indicates that a sample is less stable, and that the structure breaks down more easily than a sample with a longer LVR (higher critical stress).

Sample	Critical stress (Pa)
Reference 705 with Binder 2	4.4
705 with Binder 15	4.7

TABLE 12
CRITICAL STRESS OF REFERENCE 705 WITH BINDER 2 AND 923 WITH BINDER 15.

The critical stress of the two samples are given in Table 12. Reference 705 with Binder 2 had a critical stress of 4.4 Pa, which was slightly lower than that of 705 with Binder 15. Plotting tan δ showed (Image 15) that 705 with Binder 15 was more elastic than reference 705 with Binder 2, indicating that reference 705 with Binder 2 had a less structured and more fluid behavior in the measured stress interval, i.e. that Binder 15 was slightly more stable than the reference.

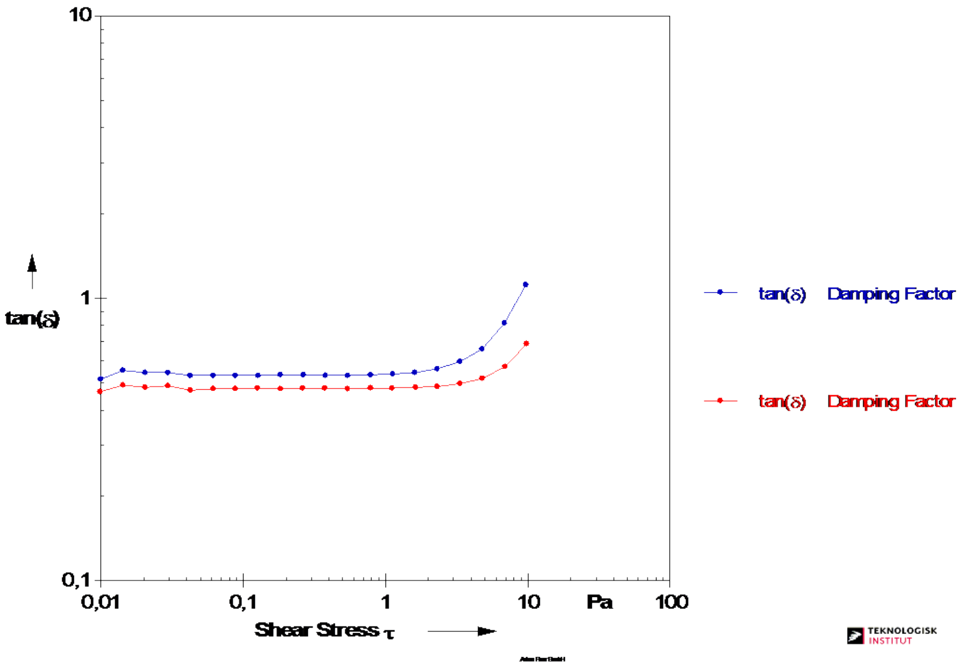

IMAGE 15
TAN δ AS A FUNCTION OF STRESS OF REFERENCE 705 WITH BINDER 2 (BLUE) AND 705 WITH BINDER 15 (RED).

Frequency sweep
The frequency sweeps showed time-dependent behavior. Short-term behavior is simulated at high frequencies, whereas long-term behavior is simulated at low frequencies, i.e. low frequencies may indicate storage stability, but higher frequencies indicate stress impact of the sample and may compare to the accelerated test by increasing the temperature of the sample. The frequency sweeps for the formulations are shown in Image 16, where it was observed that both samples were dominated by a higher G' in the entire frequency area.

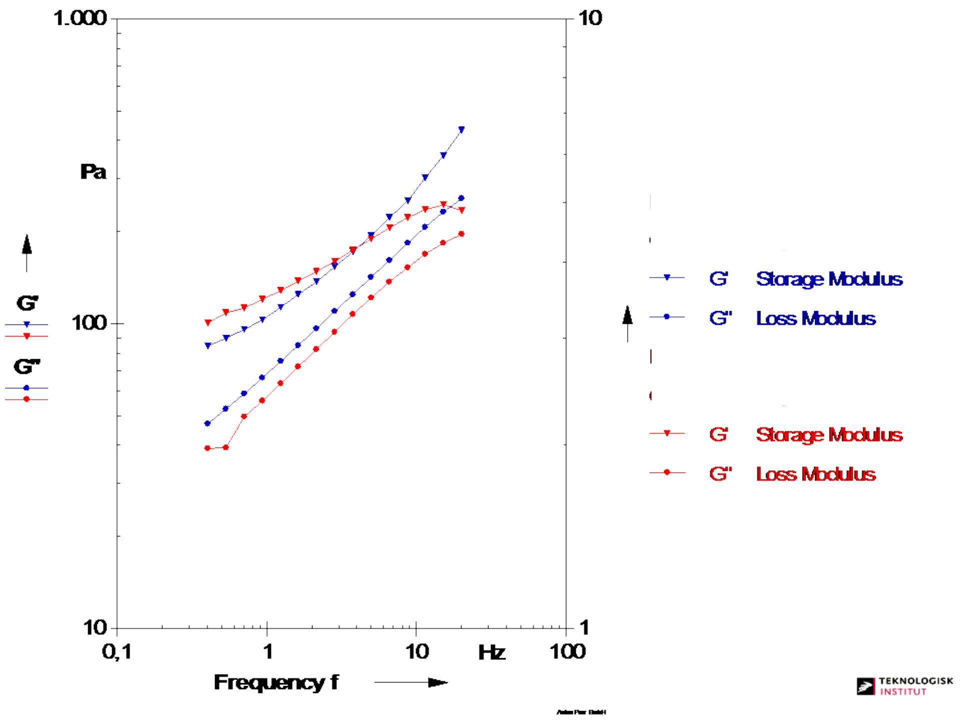

IMAGE 16
FREQUENCY SWEEPS OF REFERENCE 705 WITH BINDER 2 (BLUE) AND 705 WITH BINDER 15 (RED).

Tan δ is shown as a function of frequency in Image 17. At the lower frequencies, 705 with Binder 15 showed more elastic behavior than reference 705 with Binder 2, and reference 705 with Binder 2 showed a less structured, more fluid behavior than 705 with Binder 15. At higher frequencies (>10 Hz) they shifted, and 705 with Binder 15 showed a less structured, more fluid behavior than reference 705 with Binder 2.

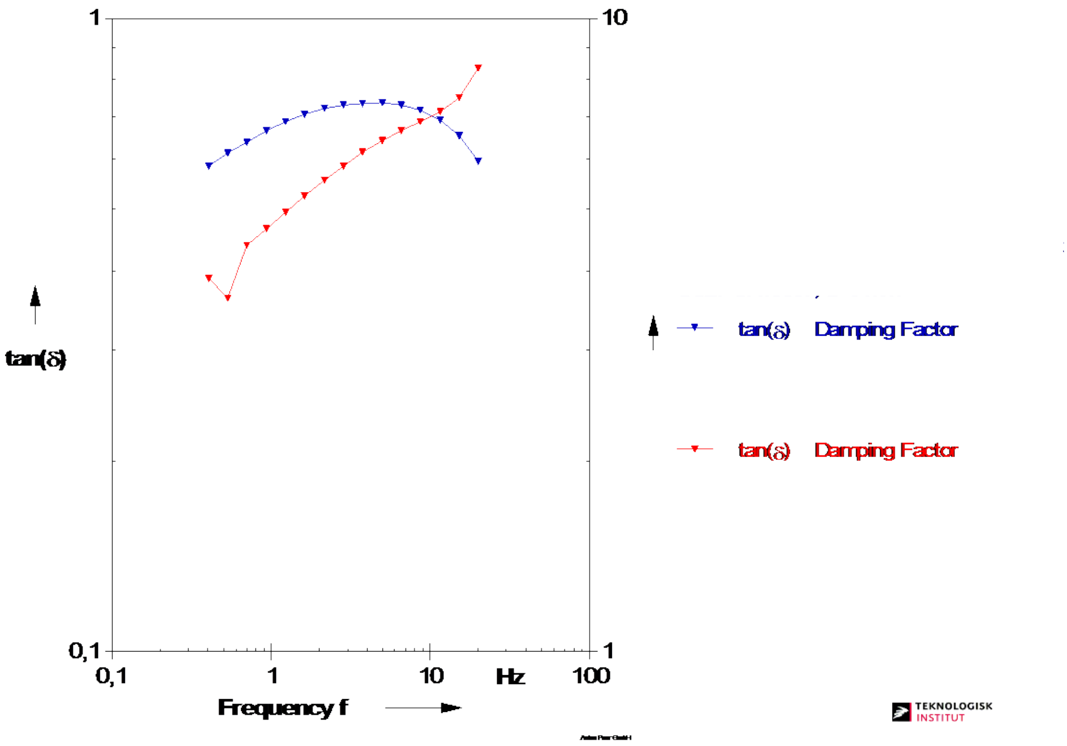

IMAGE 17
TAN δ AS A FUNCTION OF FREQUENCY OF REFERENCE 705 WITH BINDER 2 (BLUE) AND 705 WITH BINDER 15 (RED).

Conclusion on stability analyses

Stress and frequency sweeps were used to characterize the stability properties of the reference system 705 with Binder 2 and the alternative system 705 with Binder 15. Overall, the results showed that 705 with Binder 15 was more elastic – i.e., more stable – than reference 705 with Binder 2 in the measured stress range and at the lower frequencies. The reference 705 with Binder 2 showed, thus, a less structured, more fluid (less stable) behavior in the measured stress interval and at the lower frequencies, but became more elastic and less viscous than 705 with Binder 15 at the higher frequencies, i.e. it was more stable than 705 with Binder 15 at higher frequencies. The rheological results thereby indicated a behavior comparable to what was observed when traditional stability tests were used, meaning that the rheological measures may be used to foresee the stability faster than when traditional storage at different temperatures is used.

To avoid the coagulation of 705 with Binder 15 at elevated temperatures, the formulation was optimised, which again requires stain-blocking tests to ensure basic performance.

5.2.3 Optimisation of sealing effect and formulation stability

As experiments showed the need to add an emulsifier to increase the stability of the Binder 15-based system, a series of stain-blocking tests with varying amounts of emulsifier were carried out. In Image 18 below, the results of these tests can be seen indicating a decrease in visual blocking with increasing addition of the emulsifier. 2% was chosen as the concentration for further studies, as this was the smallest amount needed to obtain the desired stability.

Binder 2 | 3.5% emulsifier 1 | 2.0% emulsifier 1 | 2.75 % emulsifier 1

IMAGE 18
VISUAL BLOCKING TESTS OF SEALING PRIMER WITH BINDER 15 AND VARYING AMOUNTS OF EMULSIFIER (INDICATED AS % BELOW THE IMAGE). ON THE LEFT IS THE REFERENCE SEALING PRIMER WITH BINDER 2.

5.2.4 Sensory evaluation test of and VOC emission from sealing primer

A reference / benchmark study was conducted for the sensory evaluation of the sealing primer with Binder 2 using the methodology described in section 2.2.5. Three types of test specimens were prepared:

- Heat-treated wood (HTW)
- HTW painted with sealing primer 705 with Binder 2, white
- Sealing primer 705 with Binder 2 on glass

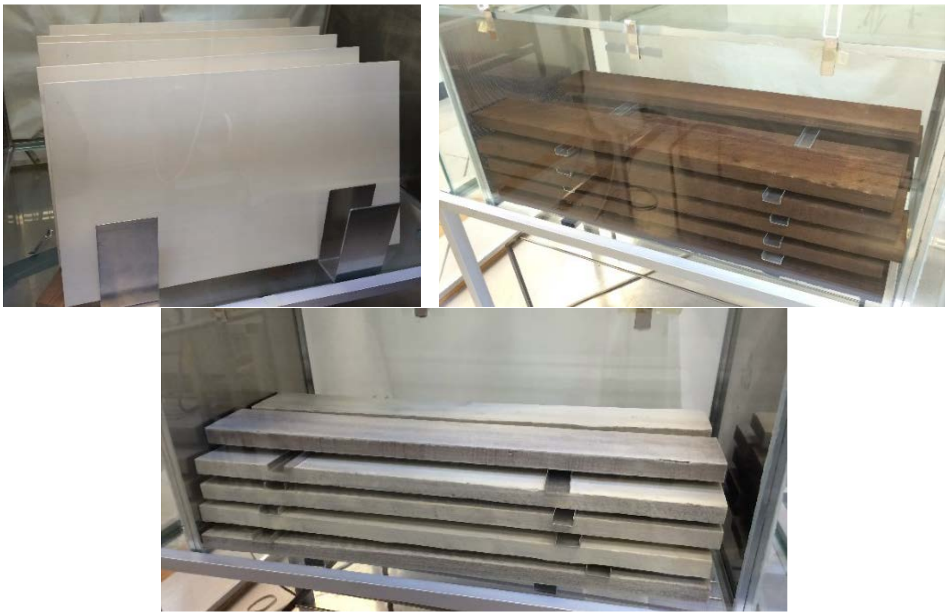

IMAGE 19
TOP LEFT: SEALING PRIMER 705 WITH BINDER 2 ON GLASS IN 700 L CLIMPAQ. TOP RIGHT: HTW IN 200 L CLIMPAQ. BOTTOM: HTW WITH SEALING PRIMER WITH BINDER 2 IN 200 L CLIMPAQ.

The sensory panel evaluated acceptance and intensity of the reference specimens after three, seven and 28 days of conditioning, and the results are given in Table 13.

	HTW		HTW 705 + BINDER 2		705 + BINDER 2 on glass	
Days	**A / I**	**Evaluation**	**A / I**	**Evaluation**	**A / I**	**Evaluation**
3	-0.80	Clearly unacceptable	-0.10	Just unacceptable	0.90	Clearly acceptable
	4.5	Overwhelming	2.5	Moderate-strong	0.4	No/weak odour
7	-0.80	Clearly unacceptable	0.10	Just acceptable	0.83	Clearly acceptable
	4.0	Very strong	2.0	Moderate	0.6	No/weak odour
28	-0.30	Unacceptable	0.10	Just acceptable	0.90	Clearly acceptable
	3.0	Strong	2.0	Moderate	0.6	No/weak odour

TABLE 13
SENSORY EVALUATION RESULTS OF REFERENCE SEALING PRIMER WITH BINDER 2 (705 + BINDER 2). A / I: ACCEPTANCE/INTENSITY MEASURES.

The sensory evaluation results indicated that the odour from HTW was unacceptable with very strong intensity, whereas odour from the reference sealing primer was clearly acceptable with no/weak intensity. The sealing primer with Binder 2 sealed odour emissions from HTW with the same sensory evaluation result after seven and 28 days, but did not fully block odour after three days. This demonstrated that seven days was an appropriate duration for evaluating sealant effectiveness towards odour from HTW when using the sealing primer with Binder 2 as a benchmark; however, a detailed comparison of sealing primers with alternative binders would benefit from more frequent evaluations.

To support the sensory evaluation, determination of VOC emissions from HTW painted with sealing primer with Binder 2 was carried out according to the method described in section 2.2.6. The concentrations in the Climpaq exhaust air of the main volatile organic compounds (VOCs) and carbonyls after 28 days are given in Table 14.

Substance	CAS no.	HTW (µg/m³)	HTW 705 + BINDER 2 (µg/m³)	HTW odour relevant[2]
Aldehydes				
Formaldehyde[1]	50-00-0	6	1	No
Acetaldehyde[1]	75-07-0	17	13	Yes
Propanal[1]	123-38-6	5	1	Yes
Hexanal[1]	66-25-1	6	1	Yes
Heptanal	111-71-7	1	nd	No
Acids				
Acetic acid	64-19-7	1170	140	Yes
Propanoic acid	79-09-4	17	nd	Yes
Butanoic acid	107-92-6	<1	nd	Yes
Pentanoic acid	109-52-4	3	nd	Yes
Alcohols, ketones, ethers, esters				
2-Propanone, 1-hydroxy-	116-09-6	50	nd	-
2-Butanone, 3-hydroxy-	513-86-0	6	nd	-
1-Pentanol	71-41-0	14	nd	No
2-Propanone, 1-(acetyloxy)-	592-20-1	2	nd	-
2-Heptanone	110-43-0	2	nd	No
Hexanoic acid, methyl ester	106-70-7	7	1	-
2,5-Hexanedione	110-13-4	2	nd	-
Guaiacol (Phenol-2-methoxy)	90-05-1	8	nd	Yes
Furfural-related				
3(2H)-Furanone, dihydro-2-methyl-	3188-00-9	3	nd	-
Furfural (2-Furaldehyde)	98-01-1	1100	195	Yes
2-Acetylfuran (Ethanone,1-(2-furanyl)-)	1192-62-7	96	9	-
Butyrolactone (2(3H)-Furanone, dihydro-)	96-48-0	6	nd	-
Methylfurfural (5-Methyl-2-furaldehyde)	620-02-0	58	nd	-
Terpenes				
Alpha-Pinene	80-56-8	1	2	No
3-Carene	13466-78-9	3	nd	No
d-Limonene	5989-27-5	3	1	No

Sum of other terpenes		9	5	-
Paint-related substances				
2-Butenoic acid, 2-methylpropyl ester	73545-15-0	nd	1	-
Ethanol, 2-(2-butoxyethoxy)-	112-34-5	nd	7	-
Propanoic acid, 2-methyl-, 2,2-dimethyl-1-(2-hydroxy-1-methylethyl)propyl ester	74367-33-2	nd	94	-
Propanoic acid, 2-methyl-, 3-hydroxy-2,4,4-trimethylpentyl ester	74367-34-3	nd	182	-
Others				
Dodecane	112-40-3	1	2	No
Undecane	1120-21-4	2	2	No
Sum of unidentified VOCs	-	17	2	-
Total volatile substances	**-**	**2615**	**659**	
Total volatiles without paint VOCs	**-**	**2615**	**375**	

[1] *Carbonyls measured by DNPH – HPLC.*

[2] *Concentration of the VOC found in HTW is near or above the odour threshold (Gemert 2011).*
All volatile substances are determined as toluene equivalents.

TABLE 14
MEASURED VOLATILE SUBSTANCES (VOC) AFTER 28 DAYS FOR HTW AND HTW PREPARED BY SEALING WITH THE SEALING PRIMER WITH BINDER 2 (705 + BINDER 2).

The individual VOC emissions were significantly reduced, when sealing primer with Binder 2 was applied to the HTW. The overall total volatile organic compound (TVOC) emission from HTW (without paint-related VOCs) was reduced by 86%.

According to a previous study of heat treatment of Scots pine by Manninen et al. 2002, only very low concentrations of terpenes were detected, and aldehydes and carboxylic acids were the main compound classes identified. The degradation profile differed due to the lower temperature used for heat treatment in this study. The hydrothermal and acidic degradation of hemicellulose pentose and hexose sugars resulted in formation of furfural and methylfurfural.

The main substances were acetic acid, furfural and methylfurfural. Previous studies of HTW have also demonstrated the presence of the volatile substances acetic acid, furfural, methylfurfural (Esteves and Pereira, 2009; Manninen et al, 2002). Hydroxyacetone (2-propanone, 1-hydroxy-) is a carbohydrate degradation product.

The main volatile substances and the many other identified VOCs are also odour relevant, i.e., aldehydes, carboxylic acids and furane derivatives. The concentrations of the volatile substances found in HTW were near or above the odour threshold (Gemert 2011). The lignin degradation product guaiacol has an odour threshold of less than 1 µg/m^3.

Comparative testing of two sealing primers with Binder 15 plus 2.0w% emulsifier and Binder 15 plus 2.75w% emulsifier, respectively, as alternatives to the sealing primer with Binder 2 were performed by sensory evaluation. All formulations were tested with application of the same amount of 7 L/m^2 sealant on HTW.

The results of the sensory evaluation are shown in Image 20, and the results of the volatile compound emissions are shown in Table 15. The results from the sensory evaluation showed that the Binder 15-containing alternatives block odours and emissions; however, they may not be as efficient as the sealing primer with Binder 2. However, the deviations of the sensory evaluation were significant and leave the question whether the data are inconclusive.

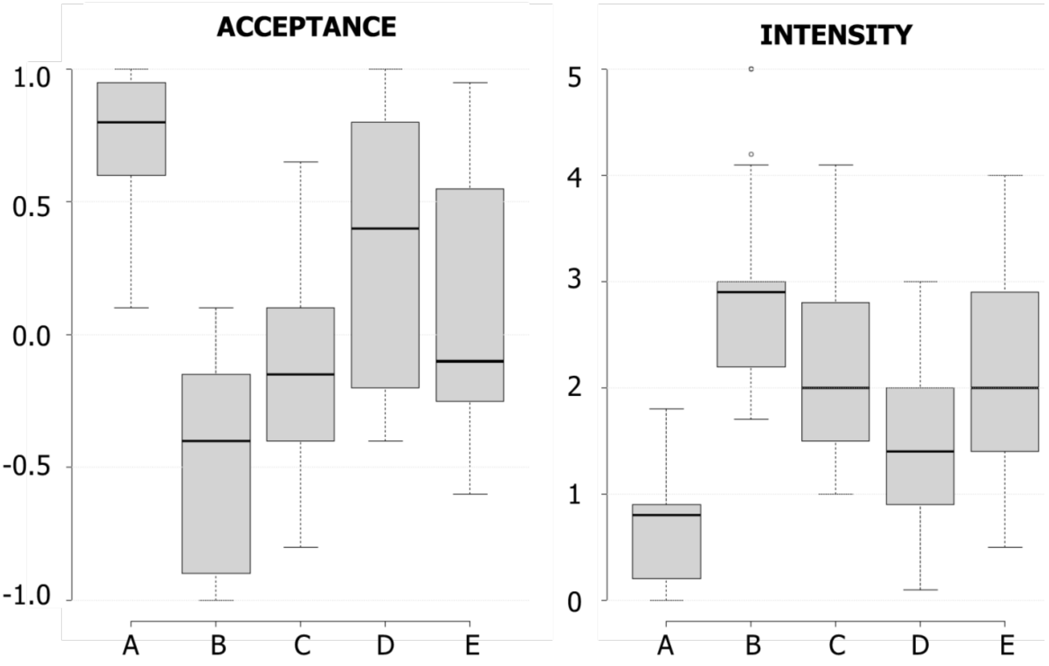

IMAGE 20
SENSORY EVALUATION OF ODOUR ACCEPTANCE AND INTENSITY. BOX PLOTS OF OBSERVATIONS AND MEDIAN VALUES FROM LEFT TO RIGHT: (A) EMPTY REFERENCE, (B) HTW AND (C) 705 WITH BINDER 15 WITH BINDER 15 + 2.75W% EMULSIFIER ON HTW, (D) 705 WITH BINDER 15 WITH BINDER 2 ON HTW, (E) 705 WITH BINDER 15 + 2.0W% EMULSIFIER ON HTW.

The results from the VOC measurements from the Climpaq air in Table 15 showed that all sealing primers efficiently blocked the emissions of volatile substances. The sealing primer with Binder 2 totally blocked the emission of acetic acid and furfural. In comparison with the prevoiusly described screening for odour retention by sealing primer with Binder 2 (Table 13), the HTW wood slab surfaces were plained before application of the sealants, and, therefore, the blocking effect wass more apparent due to the even and smooth surface.

The alternatives also efficiently blocked the emissions of VOC and the two alternatives were shown to have approximately the same blocking effect. Texanol emitted from the HTW painted with 705 with Binder 2, whereas texanol was not found in emissions from the HTW painted with sealing primers with Binder 15. Propanediol was found instead of texanol from the Binder 15-containing alternatives.

Substance	CAS-no.	HTW (µg/m³)	HTW 705 + BINDER 2 (µg/m³)	HTW 705 + BINDER 15 (2.0%) (µg/m³)	HTW 705 + BINDER 15 (2.75%) (µg/m³)
Aldehydes					
Formaldehyde[1]	50-00-0	10	1	2	1
Acetaldehyde[1]	75-07-0	7	3	5	5

Butanal[1]	-	3	1	1	1
Hexanal	66-25-1	26	1	2	2
Acids					
Acetic acid	64-19-7	7521*	-	38	44
Propanoic acid	79-09-4	167	-	-	-
Propanoic acid, 2-methyl-	79-31-2	7	-	-	-
Pentanoic acid	109-52-4	4	-	-	-
Hexanoic acid	109-52-4	43	-	-	-
Alcohols, ketones, ethers, esters					
Acetone	67-64-1	23	2	4	4
2-Propanone, 1-hydroxy- (Tol eq)	116-09-6	1	-	-	-
1-Butanol	71-36-3	3	-	1	1
Guaiacol (Phenol-2-methoxy) (Tol eq)	90-05-1	5	-	-	-
Furfural-related					
Furfural (2-Furaldehyde)	98-01-1	1247	3	13	15
Butyrolactone (Tol eq)	96-48-0	4	-	-	-
Terpenes					
Alpha-Pinene	80-56-8	7	2	3	2
3-Carene	13466-78-9	21	1	3	2
d-Limonene	5989-27-5	9	1	1	1
Others					
m,p-Xylene	179601-23-1	11	1	2	2
o-Xylene	96-48-0	7	1	1	1
Benzene, 1,3,5-trimethyl	108-67-8	2	-	-	-
p-Cymene (Tol eq)	99-87-6	5	-	1	-
Undecane	1120-21-4	12	2	2	3
Dodecane	112-40-3	3	4	1	2
Paint-related substances					
Propylene glycol	57-55-6	-	-	33	38
Ethanol, 2-(2-butoxyethoxy)-	112-34-5	-	25	16	19
Texanol	25265-77-4	-	125	-	-

Total volatile substances	-	**9148**	**173**	**129**	**143**
Total volatiles without paint VOCs	-	**9148**	**23**	**80**	**86**
TVOC (ISO 16000-6)		**1515**	**157**	**100**	**108**

[1] *Carbonyls measured by DNPH – HPLC.*
* Measurement exceeds highest quantitation level
Tol eq = quantified as toluene equivalent

TABLE 15
MEASURED VOLATILE SUBSTANCES AFTER 8 DAYS (CLIMPAQ) OF HTW AND HTW PAINTED WITH 2 LAYERS OF (A) SEALING PRIMER WITH BINDER 2, (B) SEALING PRIMER WITH BINDER 15 + 2.0W% EMULSIFIER AND (C) SEALING PRIMER WITH BINDER 15 + 2.75W% EMULSIFIER.

The results slightly indicated that the primer with Binder 15 and 2.0w% emulsifier performed better than the primer with 2.75w% emulsifier.

Also, the results indicated that this primer may need an extra layer to match the existing 705 with Binder 2. For this reason, comparative emission testing of volatile compounds was performed in a climate chamber with HTW samples applied with three layers of 705 with Binder 15 and 2.0w% emulsifier to HTW (total 78 µm) and two layers of 705 with Binder 2 on HTW (total 57 µm), respectively. The film thickness of sealing primers appears in Table 16.

Sample	Load (m^2/l)	Layers	Thickness (µm)	Standard deviation (%)	Average thickness (µm)
Sealing primer with Binder 2 (Climpaq)	7	2	58 57 50	9 13 12	55
Sealing primer with Binder 15 + 2.0w% emulsifier (Climpaq)	7	2	50 52 57	11 16 13	53
Sealing primer with Binder 15 + 2.75w% emulsifier (Climpaq)	7	2	46 50 55	8 7 4	50
Sealing primer with Binder 2 (Chamber)	7	2	56 59 56	9 11 9	57
Sealing primer with Binder 15 + 2.0w% emulsifier (Chamber)	4.7	3	76 78 79	9 24 13	78

TABLE 16
EN 92 7-5 FILM THICKNESS ON HTW OF SEALING PRIMERS WITH VARYING BINDERS. AVERAGE OF FIVE MEASUREMENTS ON THREE SAMPLES EACH.

The differences in film thickness may explain the slight variation in the sensory evaluation results and the chemical analyses. The thicker film (78 µm) with application of an extra layer of 705 with Binder 15 and 2.0w% emulsifier resulted in the same retention of VOCs as two layers of 705 with Binder 2 (57 µm). The VOC emission results are given in Table 17.

In addition to the emission data, it was observed that the surface of the sealing primers with Binder 15 were non-sticky in comparison with the existing sealing primer with Binder 2. When the slabs of HTW treated with Binder 2-containing primer were stored after the emission tests, the wood slabs stuck together.

Substance	CAS no.	HTW (µg/m³)	HTW 705 + BINDER 2 (µg/m³)	HTW 705 + BINDER 15 (2.0%) (µg/m³)
Aldehydes				
Formaldehyde[1]	50-00-0	6	1	1
Acetaldehyde[1]	75-07-0	5	1	2
Hexanal	66-25-1	33	1	1
Acids				
Acetic acid	64-19-7	5430	-	-
Propanoic acid	79-09-4	115	-	-
Propanoic acid, 2-methyl-	79-31-2	4	-	-
Hexanoic acid	142-62-1	7	-	-
Alcohols, ketones, ethers, esters				
Acetone	67-64-1	10	3	4
2-Propanone, 1-hydroxy- (Tol eq)	116-09-6	5	-	-
1-Butanol	71-36-3	2	-	-
Guaiacol (Phenol-2-methoxy) (Tol eq)	90-05-1	3	-	-
Furfural-related				
Furfural (2-Furaldehyde)	98-01-1	716	3	1
Butyrolactone (Tol eq)	96-48-0	4	-	-
Methylfurfural (Tol eq)	620-02-0	8	-	-
Terpenes				
3-Carene	13466-78-9	4	-	-
Others				
m,p-Xylene	179601-23-1	3	-	-
o-Xylene	96-48-0	4	-	-
Benzene, 1,3,5-trimethyl	108-67-8	2	-	-
p-Cymene (Tol eq)	99-87-6	2	-	-
Undecane	1120-21-4	2	-	-
Dodecane	112-40-3	2	-	-

Paint-related substances				
Propylene glycol	57-55-6		-	111
Ethanol, 2-(2-butoxyethoxy)-	112-34-5	-	43	25
Texanol	25265-77-4	-	220	-
2-propanol, 1-(2-methoxypropoxy)-	13429-07-7		-	2
Total volatile substances	**-**	**6367**	**272**	**147**
Total volatiles without paint VOCs	**-**	**6367**	**9**	**9**
TVOC (ISO 16000-6)	**-**	**1269**	**154**	**43**

[1] *Carbonyls measured by DNPH – HPLC.*

Tol eq = quantified as toluene equivalent

TABLE 17

MEASURED VOLATILE SUBSTANCES AFTER 7 DAYS (CHAMBER).

6. Health and environmental assessment of alternative binders

6.1 Approach

A health and environmental (H&E) assessment is a vital part of working in the paint industry, and Beck & Jørgensen undertake a specific approach, when they consider which new raw materials are under consideration for use in their products.

The approach interacts closely with technical assessments, reflecting the most efficient approach so a complete H&E assessment does not need to be carried out for material that fails the first technical evaluation, or the reverse. For each material, the most efficient approach is estimated based on the availability of information on both H&E and technical data as well as the cost (time or economic) of obtaining more knowledge (supplier contact, analyses, tests, etc.). For this reason, the level of information may differ significantly; however, it is very important that raw materials introduced in products are adequately assessed with respect to H&E as well as to the technical performance in the product.

A combination of the working report *Substitution of alkylphenol ethoxylates (APEOs) in paint, wood protection, glue and sealant* (Rasmussen 2003) and internal methods at Beck & Jørgensen has formed a basis for how to conduct the H&E assessment of the alternatives. A general problem related to this kind of substitution efforts is that the full ingredients list of the mixtures used as raw material is most often not provided by the supplier. However, as much information as possible has been collected from the supplier as well as from other sources. Specifically, when conducting H&E assessments at Beck & Jørgensen, their primary effort is to study differences between the complete formulations of the alternatives compared to the current binder systems.

Primarily, the following information has been sought for:

- Material safety data sheet (MSDS) and safety data sheet (SDS)
- Content of SVHCs
- Identity and content of preservatives
- The type of alternative surfactants used

Therefore, the underlying basis is the available information on the components of each alternative binder mixture, and for health and environmental assessments, some basic examples of information collected about the surfactant used in alternative binders are given in Table 18. Unfortunately, experience has shown that especially information on the surfactant in the alternative binders is difficult to obtain due to this being a vital parameter for the competitiveness of the products.

Environment	Health
SDS for the raw material for same or related products	Updated SDS

Search in databases and handbooks	Information on surfactant from supplier, e.g.: • Type of surfactant • Chain length • EO level
Search in primary literature	

TABLE 18
EXAMPLES OF BASIC INFORMATION FOR H&E ASSESSMENT OF THE TENSIDES IN BINDER ALTERNATIVES.

From the Safety Data Sheets (SDS or MSDS) a new ingredient was evaluated to identify:

- If the ingredient is classified within CLP[1] (the CLP Regulation: Classification, Labelling and Packaging)
- Which chemical components is found in the ingredient:
  - Does the ingredient contain any classified (CLP) components?
  - Does the ingredient contain components known as CMR[2], SVHC or PBT compounds?
  - Does the ingredient contain compounds that are problematic in relation to a product evaluation ("*Gravide malere-ordning*") regarding components of risk to pregnant painters offered by *Arbejdsmiljøhuset*[3]
  - Does the ingredient contain components that are problematic in relation to MAL codes[4]? MAL code should be kept at "00-1".
  - Does the ingredient contain components that have been or are part of existing environment and working environment goals in Beck & Jørgensens occupational health and safety management system (OHSAS 18001/ISO 14001)? These are environmental goals updated yearly to reduce their impact on employees and the environment set up by Beck & Jørgensen as a part of their certified ISO 14001 system, stating among other things, that Beck & Jørgensen will not discharge APEO-containing wastewater.
- Which amount of VOCs are contained within the ingredient? Ensure compliance with the VOC directive.
- Which amount of VOCs and SVOCs are contained within the ingredient? Is there compliance with limits for indoor environment in the coming EU Ecolabel (Blomsten)?

On the basis of these evaluations, calculations were made on the products containing the new ingredient. These were made to ensure:

- That the classification of the alternative product is as low as possible and not more severe than that of the substituted product, which is subjectively evaluated
- That the MAL code is as low as possible (not exceeding the substituted product)
- That the product can be used indoors by pregnant painters
- Compliance with the VOC directive and that the amount of VOCs are lower than for the product that is substituted
- That EUH208 sentences[5] are constant or fewer, as far as possible
- Approval for EU Ecolabel (Blomsten) achievable if the substituted product was approved

6.2 H&E evaluation of binders for industrial primer

As alternatives for Binder 1 in the industrial primer systems at Beck & Jørgensen, three possible candidates were identified. In Table 19 below, the basis for evaluation of these alternatives is listed according to the criteria listed in section 6.1.

[1] For further information, see: http://echa.europa.eu/web/guest/regulations/clp
[2] Carcinogenic, mutagenic or toxic to reproduction
[3] http://www.am-huset.dk/raadgivning/kemisk-biologisk-arbejdsmiljoe/gravid-paa-arbejde/
[4] A code advising painters on the use of personal protective equipment to avoid health risks during use of the product. 00-1 is the lowest and safest code for products, http://mst.dk/groenne-tips/hjemmet/faktaark/mal-koder-faktaark/, http://arbejdstilsynet.dk/da/regler/bekendtgorelser/a/sam-arbejde-med-kodenummerede-produkter-302-.
[5] EUH208: declaration of sensitiser. Attributed at content of classified sensitiser at 1/10 of classification limit.

Here it was obvious that Binder 3 from Supplier 1 was the preferred substitute for Binder 1, if it was possible to obtain a stable formulation without addition of other problematic substances. From this evaluation, the alternative Binder 5 was discarded as a substitution for the existing binder system

	Binder 1	**Binder 3**	**Binder 5**
Is the ingredient classified within CLP?	No	No	Skin Corr./Irrit. 2 Eye Dam./Irrit. 2
- Does the ingredient contain any classified (CLP) components?	Nonylphenol, ethoxylated (9016-45-9)	No	Stainblocking additive 2 2-(2-Butoxyethoxy)-ethanol Ammonium
- Does the ingredient contain components known as CMR, SVHC or PCB compounds?		No	No
- Does the ingredient contain compounds problematic in relation to ***Arbejdsmiljøhusets*** "Gravide malere-ordning"?		N/A*	Yes, but not critically[6]
- Does the ingredient contain components problematic in relation to MAL codes? MAL code should be kept at "00-1".		No	No
Does the ingredient contain biocides	1,2-benzisothiazol-3/2H)-on	A 3:1 mixture of 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one (11 ppm)	1,2-Benzisothiazolin-3(2H)-one (55 ppm) 2-Methyl-2H-isothiazolin-3-one (51 ppm) A 3:1 mixture of 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one (11 ppm)
- Does the ingredient contain components that have been or are part of existing environment and working environment goals in B&J's occupational health and safety management system (OHSAS 18001/ISO 14001)?		No	$Zinc^{2+}$, tetraammine-, hydroxide (1:2), (T-4)-, (up to 2%) (may be a list A compound, i.e., relevant to avoid in the wastewater)
Which amount of VOCs are contained within the ingredient and is this in	N/A*	N/A*	22000 mg/kg, the binder will be part of a product category with maximum allowed VOC levels of

[6] The compound is mentioned in the "*Gravide malere-ordning*" from Arbejdsmiljøhuset, but without a definit limit.

compliance with the VOC directive?			30 g/l
Which amount of VOCs and SVOCs are contained within the ingredient to ensure compliance with limits for indoor environment in the coming EU Ecolabel (Blomsten)?	N/A*	N/A*	N/A*

TABLE 19
H&E ASSESSMENT OF THE REFERENCE AND ALTERNATIVE BINDERS FOR THE INDUSTRIAL PRIMER. (*) N/A: NOT AVAILABLE

The H&E assessment of the temporary alternative to Binder 1, namely Binder 7, is listed below. From the data, it is evident that Binder 7 alone is a preferred alternative to Binder 3, but the need for the additive Stainblocking additive 1 in order to obtain the desired primer properties is not desirable.

	Binder 1	Binder 7	Stainblocking additive 1
- Does the ingredient contain any classified (CLP) components?	Nonylphenol, ethoxylated (9016-45-9)	No	Sodium aluminate (10-25%) Sodium hydroxide (2.5-10%) Triethanolamine (10-25%)
Is the ingredient classified within CLP?	No	No	Skin Corr. 1A H314 Met. Corr.1, H290
- Does the ingredient contain components known as CMR, SVHC or PCB compounds?		No	No
- Does the ingredient contain compounds problematic in relation to the scheme "Gravide malere-ordning" from ***Arbejdsmiljøhuset***?		No	N/A*
- Does the ingredient contain components problematic in relation to MAL codes? MAL code should be kept at "00-1".		No	N/A*
Does the ingredient contain biocides	1,2-benzisothiazol-3/2H)-on	1,2-benzisothiazol-3(2H)-on	N/A*
- Does the ingredient contain components that have been or are		No	N/A*

part of existing environment and working environment goals in B&J's occupational health and safety management system (OHSAS 18001/ISO 14001)?			
Which amount of VOCs are contained within the ingredient to ensure compliance with the VOC directive?	N/A*	N/A*	N/A*
Which amount of VOCs and SVOCs are contained within the ingredient to ensure compliance with limits for indoor environment in the coming EU Ecolabel (Blomsten)?	N/A*	N/A*	N/A*

TABLE 20
H&E ASSESSMENT OF THE REFERENCE AND THE TEMPORARY ALTERNATIVE FOR THE INDUSTRIAL PRIMER, XK-176, ALONG WITH THE NEEDED ADDITIVE. (*) N/A: NOT AVALIABLE

6.3 H&E evaluation of binders for sealing primer

As alternative for the use of Binder 2 from Supplier 1, two alternatives were identified. One was Supplier 3 Binder 11 and the other was Supplier 6 Binder 15. Binder 11 contains a mixture of BIT, MIT and CIT/MIT and is therefore not as favorable an alternative as Binder 15, which has no classification even when mixed with the necessary emulsifier. Therefore, Binder 15 was chosen as the alternative to use in further work.

The stability tests and upscaling protocols indicated that the Binder 15 / Emulsifier 1-mixture can be substituted 1:1 with Binder 2, and, therefore, this recipe is eligible to the EU ecolabel 'Blomsten'. However, due to the cost associated with achieving this label, and the relative small production size of this primer, this will not be pursued further from Beck and Jørgensen

	Binder 2	Supplier 6 Binder 15 with Emulsifier 1	Binder 11
Is the ingredient classified within CLP?	Skin Irrit. 3, H315 Eye Irrit. 2, H319	No	No
- Does the ingredient contain any classified (CLP) components?	Nonylphenol, ethoxylated (9016-45-9)	No	No
- Does the ingredient contain components known as CMR, SVHC or PCB compounds?	N/A*	No	N/A*
- Does the ingredient contain compounds problematic in relation to the scheme "Gravide malere-ordning" from ***Arbejdsmiljøhuset***?		No	No

- Does the ingredient contain components problematic in relation to MAL codes? MAL code should be kept at “00-1”.	No	No
Does the ingredient contain biocides	No	1,2-Benzisothiazolin-3(2H)-one (140 ppm) 2-Methyl-2H-isothiazolin-3-one (95 ppm) A 3:1 mixture of 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one (13.5 ppm)
- Does the ingredient contain components that have been or are part of existing environment and working environment goals in B&J’s occupational health and safety management system (OHSAS 18001/ISO 14001)?	No	No
Which amount of VOCs are contained within the ingredient to ensure compliance with the VOC directive?	N/A*	N/A*
Which amount of VOCs and SVOCs are contained within the ingredient to ensure compliance with the limit for indoor environment in the coming EU Ecolabel (Blomsten)?	N/A*	N/A*

TABLE 21
H&E ASSESSMENT OF THE REFERENCE AND ALTERNATIVE BINDERS FOR THE SEALING PRIMER. (*) N/A: NOT AVALIABLE

7. Scale-up and technical evaluations

In general, preference is given to a new product that does not require any significant changes with regard to handling, whether it concerns preparation, equipment, application method or the like. Likewise, it is strongly preferred that technical data remain unchanged, e.g., that rheological properties are unchanged, that drying times are not prolonged and that the layer thickness is unaffected, etc. Such preferences may not all be of key importance in order to make a product function well and achieve good product performance; however, there is a strong need to align with user demands, since experience has shown a distinct lack of willingness to change working procedures in the trade. Hurdles in communicating and the need for changes in procedures may result in poor product performance and discontent with the product in the trade and among end-users.

Such challenges will always be balanced against the possible alternatives: one possibility could be to continue using the existing product (may not be an option due to regulation; may compromise company profile, CSR, etc.), to introduce a new product with reduced performance but the same handling requirements, or to introduce a substitute product with the same performance, which requires changes in working procedures. For Beck & Jørgensen, the last case will be the option of choice for the sealing primer, where three layers of sealing primer with Binder 15 are required to perform on par with the sealing primer with Binder 2 applied in two layers. This means that the 705 with Binder 15 and 2.0w% emulsifier produced and tested at laboratory scale will be scaled up.

Concerning the industrial primer, an alternative binder leading to the desired profile has not been fully evaluated at present; however, due to the need to substitute the binder Binder 1 because of the APEO content, a temporary substitution of the binder from Binder 1 with Binder 7 + Stainblocking additive 1 will be carried out at Beck & Jørgensen. This is an easy substitution for Beck & Jørgensen regarding optimization and production, which will result in a satisfactory product performance and no change of handling for users. However, the need for the stain-blocking additive Stainblocking additive 1 is undesirable due to the H&E assessment of the additive, and for this reason, development work to find a more suitable binder substitute in the industrial primer is continued. Presently, development work is proceeded with a focus on Binder 3, despite the market introduction of an industrial primer with Binder 7 and Stainblocking additive 1.

7.1 Full-scale production

For all new products, a 900 litre pilot batch production in a 1000 litre tank is carried out before full-scale production.

For scale-up of the production of the sealing primer with Binder 15 and emulsifier, there is a need to introduce an intermediate product, in which the emulsifier is dissolved in water, since Emulsifier 1 is supplied as flakes.

After production of the pilot batch, the resulting product is tested by the Beck & Jørgensen quality control (QC) laboratory according to the QC specifications. If the product does not comply with the specifications, the batch will be corrected until it complies. When the product is accepted by the QC laboratory, it is evaluated by technicians affiliated with Beck & Jørgensen, and typically, a reference product is used as benchmark. Relevant for the products in this project are of course the industrial primer with Binder 1 and sealing primer with Binder 2 as benchmark products.

When the pilot batch has been approved by the technicians, full-scale production is carried out and tested in the same way as the pilot batch, i.e., by the QC laboratory and technicians.

7.2 Technical testing of paint properties

The technicians (trained painters) will test the application properties (brush, roller or airless) and evaluate the appearance of the film after application both in the wet stage as well as after drying in comparison with the benchmark product.

Then, they will test the product as part of a system with different topcoats, with and without sanding between coats, and evaluate the final appearance of the system with respect to flow and levelling, pinholes, surface defects and stain-blocking properties. The testings include challenging systems with regard to their sensibility to different handling and use; a test leading to information on the performance of the system if it is not used as intended and recommended, e.g., application on different substrates and the results of using the system with different degrees of preparation such as cleaning and sanding, etc.

Finally, the technicians will test how easy it is to clean the spray equipment if the product (like the sealing primer 705) is cationic. This is of importance, as there is a high risk that the equipment might be blocked by coagulated material if the topcoat is anionic, which is often the case.

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Appendix 1: List of abbreviations

AP	alkylphenol
APEO	alkylphenol ethoxylate
B&J	Beck & Jørgensen
CLP	the CLP Regulation: Classification, Labelling and Packaging
CMR	carcinogenic, mutagenic or toxic to reproduction
HTW	heat-treated wood
NP	nonylphenol
NPEO	nonylphenol ethoxylate
NPEOP	nonylphenol ethoxylate phosphate
PBT	persistent, bioaccumulative and/or toxic
QC	quality control
SVHC	substance of very high concern
TVOC	total volatile organic compound
VOC	volatile organic compound
vPvB	very persistant and/or very bioaccumulative

Sundere Grundere

This report describes the work carried out to substitute alkylphenol ethoxylate (APEO) compounds in two paint primer products and the results from the work. The APEO compounds were contained in the binders used in the primers, and for this reason, a substitute for the binder systems were sought. For a sealing primer required to seal odour and prevent colour breakthrough, a binder system called Diofan P 520 was identified, and a sealing effect comparable to the primer containing APEO was achieved with minor modifications of the formulation and of use. For an industrial primer, a temporary binder substitute was identified and put to use, while work is continued after project end to validate a permanent binder substitute free of APEO with adequate health and environmental characteristics.

Rapporten beskriver undersøgelser og vurderinger gennemført i et projekt, som havde til formål at erstatte alkylphenolethoxylater i malingsprodukter med andre mere miljø- og sundhedsvenlige stoffer. Der er identificeret alternative bindere i to forseglende grundersystemer

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