

Substitution of cobalt in wood protection products

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CoMEKO – Substitution of cobalt in wood protection products

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Foreword

The project Substitution of cobalt in wood protection products funded by the Danish Environmental Protection Agency's "Miljøeffektiv Teknologi" have been carried out in the period from March 2013 to March 2015.

This report describes the project results and the methodology used in achieving these results. The purpose of the project was the reduction or elimination of Cobalt(II) and methyl ethyl ketone (MEKO) from wood protection paints. These compounds today form a very effective siccative system in many alkyd wood protection paints. However, five cobalt(II) compound are on the REACH candidates list of Substances of Very High Concern (SVHC) since they are carcinogenic and toxic to reproduction. MEKO is also classified as a suspected carcinogen (Carc. 2)

The project was carried out by Danish Technological Institute and has been headed by PhD, PMP Jacob Ask Hansen and MSc, PMP Gitte Sørensen as project managers, with significant contributions from PhD Jens Bomholdt Ravnæk from The Danish Technological Institute, and David Löf and John Weijnen from PPG industries.

To assess the progress and results of the project, a steering committee has been set up with the following members:

Annika Boye Petersen & Esra Alici Pedersen, Danish Environmental Protection Agency
Gitte Sørensen & Jacob Ask Hansen, Danish Technological Institute
David Löf, PPG Industries

Conclusion and Summary

During the course of this project, a number of possible routes to reduction and/or elimination of the use of Cobalt(II) and MEKO siccative system for wood protection products have been identified. Many of these involves a change in the physical handling of the paint products. This includes various packaging strategies inspired by the food production industry. Common for most of these strategies include systems or methodologies for eliminating the activation of the dryer system prior to opening and use of the paint. These systems were divided into systems without oxygen in the packaged product thus avoiding activation of the siccative system, and systems with physical activation after opening of the product. Common for many of these solutions are unfortunately that long-time storage after opening is no longer an option, as the stability of the system is hampered by exposure to oxygen, or the post-activation.

On the basis of this, systems that entail a controlled availability of the dryer system in the wood protection products where envisioned. These systems include new encapsulation strategies to selectively release the dryer system upon application of the paint systems.

Three encapsulation strategies where studied:

- An oil in water in oil micro emulsion, where the siccative system is separated from the continues alkyd phase of the paint system
- A core shell strategy using water based siccative systems encapsulated in core shell particles within the existing water phase of the alkyd paint
- A multi lamellar onion-like structure for further compartmentalization of the siccative containing capsules

Through these studies, very promising results was obtained, although it was not possible to make a fully stable system within the timeframe of this project. The Core-shell particle systems did show very promising stability in model systems, but a final mixture into the relevant paint mixture resulted in a less than optimal stability.

The multi lamella structures also show some very promising results, but further investigation is needed in order to reach a system that can be implemented in wood protection products. This approach is very promising, but the prize for the model systems studied is not compatible with commercial sales.

Konklusion og Sammenfatning

Gennem dette projekt er der identificeret en række muligheder for at reducere og eller eliminere brugen af kombinationen af Kobolt(II) og MEKO som sikkativ system i træbeskyttelsesprodukter. Flere af disse muligheder involverer et skift i den fysiske håndtering af malingensprodukterne, inkluderende f.eks indpakningssystemer inspireret af fødevarer industrien. Et fællestræk for mange af disse tilgangsvinkler er systemer eller metoder til at reducere aktiveringen af tørrer systemet inden åbning og brug af malingen. Disse systemer er inddelt i systemer uden ilt i det pakkede produkt, hvorved der undgås aktivering af sikkativsystemet, samt systemer med en fysisk aktivering af produktet efter åbning. Fælles for mange af disse løsninger er, at disse vil fungerer i det lukkede produkt, men ikke vil kunne sikre langtidsholdbarhed efter åbning.

For at imødekomme denne udfordring blev der i dette projekt set nærmere på mulighederne for at have en kontrolleret frigivelse af det aktive tørrer system, således at dette først træder i kraft i det øjeblik malingen bliver appliceret. Her blev der studeret nye indkapslings strategier der selektivt frigør sikkativ systemet når dette appliceres.

Tre indkapslingsstrategier blev studeret:

- Olie i vand i olie mikroemulsioner, hvor sikkativsystemer er separeret fra den kontinuere alkyd fase i maling-systemer
- En Core shell strategi, hvor der benyttes et vandbaseret sikkativsystem indkapslet i core shell partikler i den eksisterende vandfase i alkyd malingen.
- En multi-lamella lag i lag struktur, som vil sikre yderligere indkapsling af kapsler indeholdende sikkativ systemet.

Gennem disse studier er der opnået særdeles interessante resultater. Desværre har det inden for tidsrammen ikke været muligt at opnå fuldt stabilt system i den endelige maling-matrice. Udnyttelsen af core shell indkapslingsstrategien gav meget lovende resultater i model systemer, men iblandingen af disse partikler i den endelige malings blanding gav dog ikke den ønskede optimale stabilitet.

Multi-lamella systemet har ligeledes gives meget lovende indledende resultater, men det er her nødvendigt at foretage yderligere studier før denne kan implementeres i de endelige træbeskyttelsesprodukter. Strategien er meget lovende, men prisen for de nuværende model block co-polymerer er ikke kompatibel med den kommercielle salgspris.

1. Introduction

1.1 Background

The paint industry is a highly controversial industry considering the manufacturing process as well as the products and their application in the view of environmental and health effects of the constituents. For years, there has been a trend of reducing e.g. volatile organic compound (VOC) levels, and with the implementation of the REACH regulation, the trend towards products with a safer and more environmentally friendly profile has intensified. This has resulted in a mutual desire from legislative authorities as well as industry to reduce the contents of harmful and unwanted chemical substances in traditional paint and coating products.

Specifically, the reduction or elimination of cobalt(II) compounds, which are used as siccative in paint and coating products, is desirable. Today, five cobalt(II) compounds are on the REACH candidate list of Substances of Very High Concern (SVHC), since they are carcinogenic and toxic to reproduction.¹

Further, there is a desire to substitute the anti-skinning agent 2-butanone oxime, also known as methyl ethyl ketoxime (MEKO), since the volatile MEKO has a harmonized classification as a suspected carcinogen (Carc. 2) and a skin sensitizer.² MEKO forms an effective siccative system with the cobalt(II) drier by inhibiting in-can drying.

1.2 Objectives

The project aim was to substitute harmful cobalt siccatives as well as the anti-skinning agent MEKO from alkyd wood protection by the use of unconventional technologies under the requirements that overall beneficial product properties such as appropriate drying time and storage stability were maintained or improved. Alternative substances used in order to substitute cobalt and MEKO should have fewer concerns regarding human health as well as the environment.

1.3 Methodology

This project is divided into three work packages concerning:

1. Design of the siccative system and method development
2. Experiments on model systems
3. Formulation and test of wood protection systems

WP1 will be the basis for the work in the following WPs by focusing on a scientific approach for identification of possibilities for substitution of Co components and MEKO. This work will use existing sources to identify possible routes and expand these. This will be done via:

- Generation of overview of commercially available products

¹ Many cobalt(II) compounds (e.g. cobalt(II) sulphate, cobalt(II) dinitrate, cobalt(II) carbonate and cobalt(II) diacetate) are classified as Carcinogen 1B, Toxic for reproduction 1B. <http://echa.europa.eu/web/guest/candidate-list-table>

² <http://clp-inventory.echa.europa.eu/SummaryOfClassAndLabelling.aspx?SubstanceID=108832&HarmOnly=yes?Name=methyl+ethyl+ketoxime&DisclaimerAgr=Agree&ExecuteSearch=true&fc=true&lang=en>

- Literature based search on new alternatives to use for reducing the amount of Co and MEKO in paints. Here, there will be a focus on the study of mechanisms involved in drying, examples of this could be:
 - The use of Fe complexes with an alternative to MEKO
 - Addition of microdroplets of water to avoid the generation of free radicals in thereby limit skinning
 - Encapsulation of the drying compounds in a degradable shell
 - The use of UV-activated photoinitiater
 - Addition of oxygen scavengers to limit the amount of free oxygen and free radicals

Also, in WP1 relevant analytical approaches will be studies and selected to evaluate the final products.

In WP2, the selected strategies simple model systems will be used to develop the selected strategy. These systems are expected to give addition information on mechanisms for a preliminary evaluation of the selecte3d strategies

In the final part of the project (WP3), the developed strategies will be implemented in full wood protection systems for evaluation of the effects in the final products.

1.4 Structure of the report

This report is structured to reflect the work undertaken during the project, and thus divided into sections dealing with studies of the existing alkyd paints to define the framework to work within during this project, and the different chosen methodologies to eliminate or reduce the use of the Cobalt and MEKO siccativ systems

Section 2, defining the framework of operation, includes study of the effects of both the functions of the Cobalt(II) and the MEKO systems. This chapter also contains a catalogue of approaches than could be followed to reduce or eliminate the use of the Cobalt(II) and MEKO siccativ systems.

Section 3 is dedicated to the study of the water domains of the alkyd paints, as it was quickly evident, that these could provide the solution for the elimination of MEKO. If the Cobalt (or alternative) siccativ system is entrapped within the water domains, the use of MEKO as a stabilizer is no longer required. Results of a direct change of the siccativ addition methodologies are presented in section 4.

Section 5 presents the work done through this project to develop new methodologies to control the dryer availability in the alkyd phase of the paint emulsion, thus enabling the elimination of MEKO and possibly allowing for substitution of the Cobalt siccativ system.

2. Alkyd paints and their siccative systems

Traditionally, alkyd paints used to consist of some basic compounds, being the alkyd (i.e. the binder), organic solvent such as white spirit or xylene, pigments and extenders/fillers/thickeners. Further, a number of additives in smaller amounts are contained, for instance surface-active agents (e.g. surfactants, stabilisers, defoamers, etc.), driers, anti-skinning agents, UV stabilisers, biocides, rheology controllers, etc. Alkyd resins used today are typically oil- or fatty acid-modified polyesters, which are polyunsaturated to allow for cross-linking during the drying phase leading to film formation. Solvents are mainly turpentine oils and other dipentenes (Bieleman 2000; Van Gorkum and Bouwman 2005).

Today, most often alkyd paints contain water, as well, to conform to legislation requiring lower levels of VOCs, and these may be termed alkyd paints with water inclusion, or simply alkyd/water inclusion paints, which is the term used in this report. Typical alkyd/water inclusion paints contain 10-15 % of water in the liquid formulation. An example overview is given in Table 1.

TABLE 1
TYPICAL ALKYD/WATER INCLUSION PAINT COMPOSITION (VAN GORKUM AND BOUWMAN 2005).

Component	%(wt)
Binder	30
Organic solvent	27
Water	10
Pigments	19
Extenders	12
Additives	2

For alkyd/water inclusion paints, the siccatives mostly used are cobalt-based. Most often – and most effectively – cobalt siccatives are used in combination with MEKO as described in Chapter 2.1, meaning that a substitution of the cobalt drier will most likely result in the use of MEKO being redundant. Reversely, if MEKO is removed from the paint formulation, the cobalt drier will need modification or substitution to retain the siccative effect and avoid untimely film formation.

2.1 Siccative systems

Alkyds are the most dominant binders used for paints and coatings, and the alkyd oxidises upon contact with oxygen in the atmosphere, leading to cross-linkage (termed autoxidation). The autoxidation is relatively slow, but the reaction time may be increased when catalysed by a siccative (also called a drier) to achieve film drying within an appropriate time span after film application.

This autoxidation is a chemical drying that may also occur in an open or sealed can when the paint is in contact with air, thereby forming a solid barrier on top of the liquid paint formulation (called skin formation). To control this premature oxidation leading to skin formation, the siccative system is highly important. Today, often a cobalt siccative and the anti-skinning agent MEKO form the siccative system, ensuring, respectively, that film formation will actually occur after paint application and that it does not occur prematurely in the can (Bieleman 2000; Soucek, Khattab et al. 2012).

2.1.1 Cobalt siccatives and their alternatives

Typically, transition metal driers (as a salt/complex) are used for alkyd paints, and, in some cases, primary/active driers are used in combination with auxiliary driers (see Table 2), which may enhance the activity of the active drier (Bieleman 2000; Van Gorkum and Bouwman 2005).

TABLE 2
DRIER METALS (BIELEMAN 2000).

Active driers	Auxiliary driers	
Cobalt	Barium	Zinc
Manganese	Zirconium	Potassium
Iron	Calcium	Strontium
Cerium	Bismuth	Lithium
Vanadium		
Lead		

Cobalt is the most widely used primary drier metal for alkyd paints because of its excellent catalytic effect at room temperature, and it may be used with other metal driers for improved properties. Cobalt is used in concentrations of approx. 0.06 % and maximum 0.2 % (based on the binder solid content). The cobalt is used as either Co(II) or Co(III) and is combined with an acid ligand, which ensures adequate distribution in the paint and prevents loss-of-dry (loss of drying efficiency). A commonly used cobalt complex is the cobalt octoate (see Image 1), but a number of different ligands

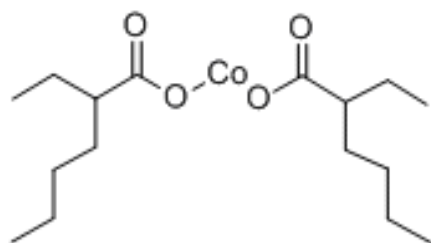


IMAGE 1
STRUCTURE OF COBALT OCTOATE.

may be used for the cobalt drier complexes. Ligand examples include e.g. 1,10-phenanthroline (phen), 2,2'-bipyridine (bipy) (see Image 2) or many different nitrogen-donor ligands, which may increase storage stability. Due to the growing concerns on the toxicity of cobalt salts and the problematic classification as carcinogens within the EU under REACH, alternatives to cobalt-based driers are highly demanded (Bieleman 2000; Pilemand, Wallström et al. 2003; Van Gorkum and Bouwman 2005; de Boer, Wesenhagen et al. 2013).

Many alternatives to cobalt-based siccatives are already offered by suppliers. Most of them are formed from the metal active driers listed in Table 2. However, cobalt is considered by far the most effective drier for air-drying alkyd paints, rendering the traditional use of other metal driers from the list in Table 2 a sub-optimal drier choice because of lower activity. The lower activity may be counteracted by increasing the amount of drier, which increases costs and may affect product performance and aesthetics. Though suppliers offer a range of different alternatives to cobalt-based

siccatives, no non-metallic compounds have been identified exhibiting sufficient siccative effect (Pilemand, Wallström et al. 2003; de Boer, Wesenhagen et al. 2013).

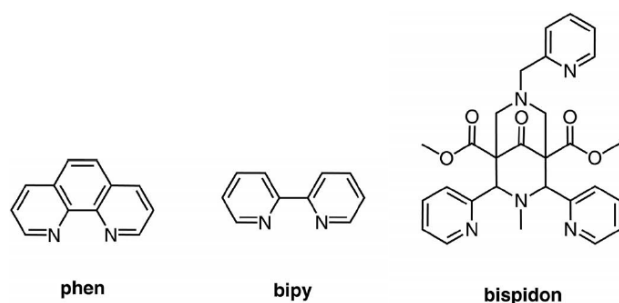


IMAGE 2
STRUCTURES OF NITROGEN-DONOR LIGAND EXAMPLES.

The search for more environmentally friendly alternatives to cobalt-based siccatives during the last decades has resulted in a number of suggested alternative compounds, many based on manganese or iron. Though alternatives to cobalt driers have in some cases reached the drier activity of the same order of magnitude as the cobalt carboxylates, they often exhibit discolouration. Recently, some iron and manganese catalysts based on polydentate nitrogen donor ligands have demonstrated performances comparable to cobalt carboxylates, including [(bispidon)Fe^{II}Cl]Cl (Fe-bispidon; Image 2). The comparable effect of Fe-bispidon in alkyds is, though, disputed by paint manufacturers, and the anti-skinning effect of MEKO (Image 3) is not sufficient when using the Fe-bispidon drier. Other alternative approaches include the combination of iron salts with a reducing agent (e.g. ascorbic acid), which however exhibits the discolouration already mentioned, and an enzymatic approach using e.g. an iron-based lipoxygenase as a drier. Surveys and reviews identifying and evaluating cobalt drier alternatives have been published over the last decade, and overall they agree that no sufficient alternatives are available (Pilemand, Wallström et al. 2003; Miccicha, Oostveen et al. 2005; Larsen and Wallström 2006; Soucek, Khattab et al. 2012; de Boer, Wesenhagen et al. 2013).

2.1.2 The siccative system with MEKO

At PPG Industries, an internal literature review has been carried out, focussed on alternatives for the anti-skinning agent MEKO. A summary with main findings and conclusions from this review is given in the section below. A more detailed discussions of the effects, probable mechanisms of and alternatives to MEKO is given in a number of surveys and papers (Bieleman 2000; Pilemand, Wallström et al. 2003; Tanase, Hierso et al. 2003; Soucek, Khattab et al. 2012). Further, a list of commercially available anti-skinning agents and their chemical characteristics is given in Table 3 below.

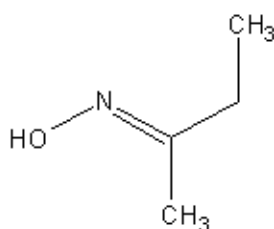


IMAGE 3
STRUCTURE OF THE ANTI-SKINNING AGENT MEKO.

A summary of MEKO as an anti-skinning agent and its alternatives

Skin formation is a common issue in alkyd paint and must be avoided, since it affects the drying properties of the paint. Anti-skinning agents are added to the formulation to counteract the skin formation, and MEKO is so far the most widely used anti-skinning agent. Unfortunately, because of its toxicity, MEKO will be under scrutiny regarding the REACH regulation, and moreover, the German authorities wish to decrease the concentration of MEKO in alkyd paint formulations. This restriction might allow a concentration of just 0.3 % MEKO in the final formulation, which is

insufficient to provide good anti-skinning properties. Today, a concentration of 1 % MEKO in the final formulation is used.

The proper mode of action of MEKO is yet unknown. Two mechanisms are considered today:

- The one, which is the most accepted, is that MEKO forms a complex with the transition ion metal of the drier, thereby inhibiting its catalytic activity. This complex is weak, and when the paint is applied, the oxime ligand evaporates and the catalytic functionality of the drier is retrieved.
- The other mechanism is a radical trap hypothesis, and is related to the antioxidant activity of MEKO. Studies are still being carried out on this subject.

These two hypotheses guide researches in a search for compounds that could possibly work in a similar fashion.

A number of alternatives to MEKO are considered among the different categories of anti-skinning agents: oximes, antioxidants and solvents. According to the literature and researchers, the oxime category seems to be the most suitable. They provide sufficient anti-skinning properties and have almost no influence on drying time, but even if all oximes are not yet classified as toxic, this could only be a matter of time.

The antioxidants provide sufficient anti-skinning properties, but, unfortunately, they retard the drying time of the paint. The converse is true for the solvents; they accelerate the drying, but provide insufficient anti-skinning properties.

Several patents claim the efficiency of alternatives with different volatility, but no general rules apply; hence, it cannot in general be said, that compounds of low volatility provide better anti-skinning properties or that highly volatile compounds have no influence on the drying time of the paint. Doubts may occur on the fact that focussing on the volatility of a compound may lead to the identification of an alternative to MEKO.

It is difficult to find a one-to-one replacement for MEKO, but suppliers are working to find the most appropriate anti-skinning agent or combination of anti-skinning agents that could provide the same properties as MEKO (San and Gabrielle 2013).

TABLE 3
COMMERCIALY AVAILABLE ANTI-SKINNING AGENTS.

Trade name	Type	Trade name	Type
Ascinin 0444	amines	Troymax anti-skin OP	cyclohexanone oxime
Ascinin 0445			
Ascinine P	2-cyclohexylphenol, 4-cyclohexylphenol	Troymax Antiskin OS	50% cyclohexanone ketoxime
Exkin 518	acetone oxime	Troymax Antiskin OL	hydroquinone
Exkin III	cyclohexanone oxime	Shamrock: Anti-skin 11	50% cyclohexanone ketoxime
Exkin OXF	DEHA, triphenylphosphite, Sr-octoate	Schwego Antigel HS	organic phosphoric acid esters

Hydroxyacetone		Schwego Antimec	alconol amine
Prevaskin MFD Prevaskin 140, 230, 320, 410, Vo8		Schwego Antimec 8010	amine
Alpamine AS	DEHA, 2-[(1-methyl-propyl)amino]ethanol	Schwego Antigel KF	alconol amine + aliphatic carboxyl ester
Borchinox 55	55 % MEKO	Schwego KF-D	aliphatic carboxyl ester
Borchinox 614	4-tert-amylphenol	Schwego Antigel	MEKO + modified phenol derivative
			2,4 pentadione

2.2 Overview of alternative approaches to avoid cobalt/MEKO siccative systems

The above review of the current situation on alternatives for the cobalt-MEKO siccative systems clearly indicates a need to explore alternatives further. This project mainly focusses on alternative approaches, meaning using metal driers other than cobalt-based driers in new ways or completely eliminating the use of metal driers by introducing new technology. The basic requirements for new compounds and new technologies are an environmentally sound profile combined with a performance at least exceeding the best available existing siccative systems used for alkyd paints today.

A brainstorm for capturing new approaches to avoid cobalt driers and/or MEKO has been carried out, and a number of the ideas have been listed in Table 4 with a few comments to each of them.

TABLE 4
ALTERNATIVE APPROACHES TO SICCATIVE SYSTEMS.

Approach	Comment
“Paint-in-bag” concept - comparable to bag-in-box wine	Possible advantages: Hinders air contact which may render MEKO superfluous; only the amount needed is tapped Possible drawbacks: Change in appearance of packaging and handling compared to traditional paints; expected lack of consumer acceptance due to changed handling/appearance; when paint has been tapped, it cannot be stored for later use; challenges with sufficient homogenisation/mixing of paint before use
Photo-initiators: WO03074466, WO2005014738, WO2007017032	Possible advantages: Perspective looks promising Possible drawbacks: Already several patents exist; the approach has been explored; the lacking commercial use indicates a not successful approach
Addition of siccative to	Possible advantages:

paint just before use

MEKO not required; technically easy solution

Possible drawbacks:

The paint cannot be stored for later use after addition of siccative because of rapid skin formation; challenges with sufficient stirring of paint before use; expected lack of consumer acceptance (for DIY) due to changed handling

Modified atmosphere/
inert gas in top of can to
avoid in-can air
exposure; possibly
combined with addition
of oxygen scavenger (in
formulation or inside
can surface)

Possible advantages:

MEKO may not be required; technically easy solution

Possible drawbacks:

The paint cannot be stored for later use after opening; may be expensive (in process)

Oxygen scavenger in
can physically located
on the inside of the can
in coating or attached
sacket

Possible advantages:

MEKO may not be required; technically easy solution

Possible drawbacks:

May not work after the can has been opened - but maybe it can be replaced; may not work if covered by the liquid paint

Protective layer formed
on top of paint by
- Whey protein
(cellulosic thickener,
briefly discussed in
Chapter 4)
- Hydro-/microgel

Possible advantages:

Will leave MEKO superfluous because of hindered air exposure;

Possible drawbacks:

Technically challenging to ensure re-formation of top protective layer after stirring/transport

Encapsulation of
siccative (discussed in
Chapter 5)

Possible advantages:

Will leave MEKO superfluous because of hindered in-can contact between siccative and alkyd

Possible drawbacks:

Technically challenging to identify encapsulation method/material that will work appropriately

3. Water domain studies

Some introductory studies to gain knowledge of the water phases and their distribution in a alkyd/water inclusion paint formulation containing 13-14 % (wt) water was carried out in the laboratory. This knowledge provides background for evaluating some of the possible solutions to the challenges addressed in the project.

3.1 Objectives of water domain studies in alkyd/water inclusion paints

In order to substitute cobalt and/or MEKO from the alkyd/water inclusion paint, a range of questions regarding the system that needed investigation were identified. Over time and with the increasing understanding of the system and the obstacles in relation to the substitution, more investigations have been included to provide the knowledge needed to approach the search for alternative siccative systems best possible.

A study of the water domains in existing traditional solvent-borne alkyd paint are required in order to find out:

- a. How the water domains are distributed in the bulk
- b. Are the water domains completely separated?
- c. Is the water a part of the continuous phase?
- d. Does water exist in a stable phase/stable domains in the alkyd/water inclusion paint?

3.2 Results of water domain studies in the alkyd/water inclusion paints

In order to answer the questions regarding the distribution of water/water domains in the traditional solvent-borne alkyd/water inclusion paint, a representative paint was visually studied using fluorescence and phase contrast microscopy.

A commercial transparent solvent-based alkyd/water inclusion wood care/wood paint was used for the investigation of the water domains in order to allow light transmission. Initial experiments were

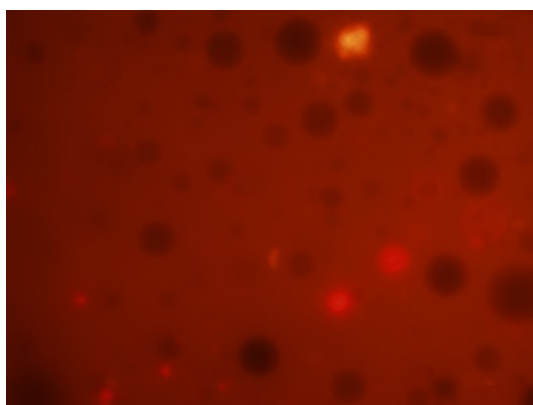


IMAGE 4
FLUORESCENCE MICROSCOPY IMAGE OF A
TRANSPARENT ALKYD/WATER INCLUSION PAINT
FORMULATION WITH ADDITION OF THE OIL-SOLUBLE
FLUORESCENT DYE, SOLVENT RED 27. THE WATER

DOMAINS ARE UNCOLORED AND APPEAR AS WATER DROPLETS THAT ARE DISPERSED IN A CONTINUOUS OIL-PHASE.

carried out in which a purely oil-soluble fluorescent dye, Solvent red 27 (Oil Red O, Sigma-Aldrich O0625), was added to a sample of the paint before investigation of the phases using fluorescence microscopy. The sample was smeared onto a glass slide in a thick layer and the sample was studied uncovered. Uncoloured droplets were observed in a continuous red-coloured phase (Image 4), suggesting that water is dispersed in a continuous oil phase (i.e. the alkyd/water inclusion paint represents a water-in-oil suspension).

Further studies using a phase contrast microscope (Malvern image analysis) were performed in order to determine the size of the water droplets and also to follow the water domains over time. In the middle of a small uncovered droplet of paint (thick film), 10-15 min. after application to the glass slide, water droplets of 5-50 μm in diameter were observed (Image 5).

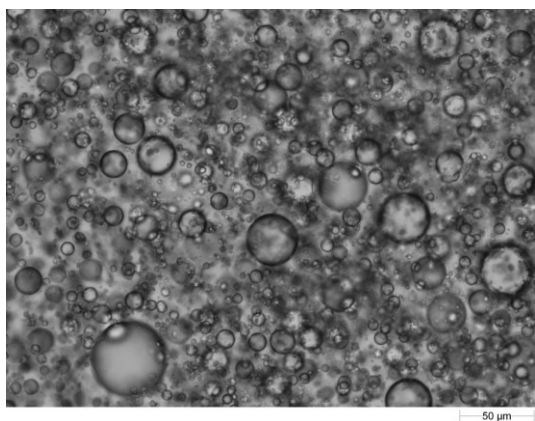


IMAGE 5
PHASE CONTRAST MICROSCOPY IMAGE OF A TRANSPARENT ALKYD/WATER INCLUSION PAINT FORMULATION. THE PICTURE IS OBTAINED FROM THE MIDDLE OF A SMALL DROPLET PAINT, 10-15MIN AFTER IT WAS PLACED ON THE GLASS SLIDE (UNCOVERED).

In a thin film of paint, smaller droplets were observed immediately after smearing of the paint on the glass slide (Image 6). The droplets were followed over time; they decreased rapidly in size and disappeared within 10 min (Image 6). A likely explanation of the apparent differences in size of the water domains in Image 5 versus Image 6 may be that smaller droplets are formed due to the mechanical force applied in order to generate a thinner film of paint. Alternatively, the difference in time of recording after application of paint onto the glass slide may affect the size of the water domains. In the beginning, the water domains may coalesce and thereby form larger domains; these domains will at some point start to decrease in size due to evaporation.

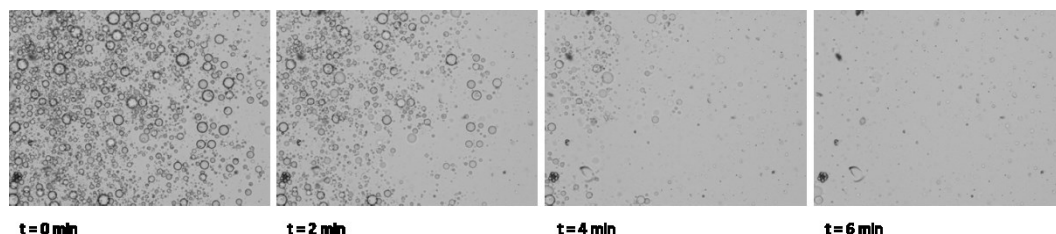


IMAGE 6
PHASE CONTRAST MICROSCOPY IMAGES OBTAINED DURING DRYING OF A TRANSPARENT ALKYD/WATER INCLUSION PAINT. THE PICTURES ARE OBTAINED FROM A THIN FILM OF PAINT RIGHT AFTER IT WAS PLACED ON THE GLASS SLIDE (UNCOVERED), RECORDINGS ARE MADE APPROX. 10 μm ABOVE THE GLASS SLIDE.

A second time lapse study of the water domains was initiated using a thicker film. This film was applied to the glass slide at the same time as the thin film that are followed over time in Image 6 but

followed from almost half an hour from application time (Image 7). Within one hour, the water is almost fully evaporated from the observed part of the film.

Microscopy of paint samples taken directly from the can without prior stirring is planned in order to establish the size of water domains in the can during long-term storage.

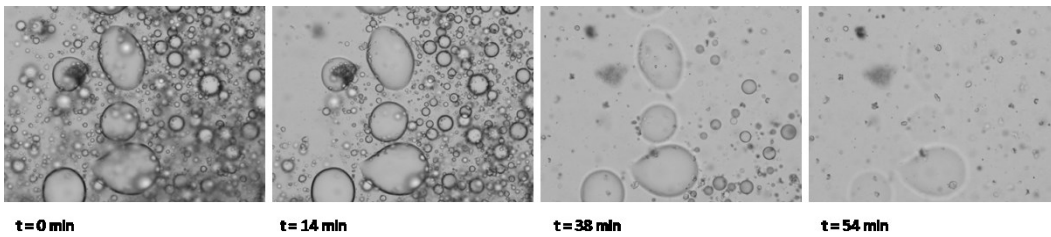


IMAGE 7
PHASE CONTRAST MICROSCOPY IMAGES OBTAINED DURING DRYING OF A TRANSPARENT ALKYD/WATER INCLUSION PAINT. THE PICTURES ARE OBTAINED FROM A THICK FILM OF PAINT ~25 MIN AFTER IT WAS PLACED ON THE GLASS SLIDE (UNCOVERED) AND FOR 1 H, APPROX. 10 μm ABOVE THE GLASS SLIDE

4. Siccative addition methodology

4.1 Objectives of the siccative addition methodology

A potential solution to the replacement of MEKO and possibly the cobalt-based drier may be the entrapment of the drier in the observed water domains. This will prevent the interaction between drier and alkyd until the drying process is desirable after paint application. Simple experiments were designed in order to evaluate the effect of dissolving different driers in the water before paint assembly and, then, to evaluate the effect on in-can skin formation.

Questions to be answered include:

- Is skin formation differently affected by addition of the drier in the solvent phase or in the water phase prior to generation of the alkyd/water inclusion paint formulation in its final state?
- Do different driers (such as driers for water- and solvent-based systems, respectively) affect the in-can drying process differently?
- Is it possible to incorporate a water-based drier in the water-phase of the alkyd paint in a stable way? And can the water selectively host the drier?

4.2 Results of studies of direct addition of siccatives to the water phase

From the microscopy images obtained in the introductory laboratory studies of a traditional alkyd/water inclusion paint it was found that the water was distributed as large micron-sized domains. As a first attempt it was decided to dilute different driers into those water domains prior to mixing with the alkyd phase.



IMAGE 8

SOLUBILITY TEST OF FOUR DRIERS. TWO ARE BASED ON COBALT COMPLEXES (A+B); ONE FOR SOLVENT-BORNE PRODUCTS (A) AND ONE FOR WATER-BORNE PRODUCTS (B). TWO OF THE DRIERS ARE BASED ON IRON (C+D); ONE INTENDED FOR WATER-BORNE PRODUCTS (C), THE OTHER FOR BOTH WATER AND SOLVENT-BORNE PRODUCTS (D).

Initially, the water solubility of four driers was tested, see Image 8. One out of the four driers, a cobalt drier for solvent-borne products based on alkyds (Cobalt Octoate, AD0039) that was included as a reference showed a very poor water solubility and was excluded from further tests. Of the remaining three, two Fe-complexes for water-borne or water and solvent-borne products based on alkyds displayed a very high water solubility (AD0037 and AD0040, respectively), while a cobalt

complex (Cobalt Octoate, ADO033) for water-borne products based on alkyds showed an intermediate water solubility.

A series of experiments were then initiated in which each of the three water-soluble driers was dissolved in the water phase prior to mixing of the water into the alkyd-containing phase; the anti-skinning agent MEKO was not included but otherwise the paint was assembled into its final state. The skin formation in-can (closed can) was then observed over a week in storage tests at room temperature and at 40 °C (accelerated storage tests). Skin formation was observed with all three driers after 24h at both temperatures; however, the skin formation was reduced in the paint formulations incorporating both of the most water soluble driers (the Fe complexes). After one week, however, the film formation appeared similar in all cans. Two reference paint formulations were included: the standard paint formulation with the Co-based drier and MEKO and a formulation without both a drier and MEKO. In both cases, the film formation was not observed. Drying was not properly prevented in-can with the driers dissolved initially in the water phase prior to mixing of the paint, apparently due to a diffusion of the drier from the water domains into the surrounding alkyd, which induced in-can film drying. The water-soluble driers used for these experiments are constituted as a complex salt, which will – not surprisingly – migrate to the surface of the water sphere and interact with the alkyd enclosing the water droplets. It is, however, worth noting that the film formation was somewhat delayed by using the most water-soluble Fe-based driers compared to the more hydrophobic driers.

In the experimental series described above, an experiment employing a cellulose thickener was included. The idea was that a jellified gel on the surface of the paint would not allow oxygen to access the paint and thus initiate radical formation and pre-mature drying in the can. Thus, a paint was assembled with inclusion of the traditional Co-based drier but without MEKO and with a further addition of a solution containing 4 % of a cellulose thickener on top of the paint. However, it appeared in the paint and after 24 h, skin formation was observed and this approach was abandoned.

5. Control of drier availability

Encapsulation of the drier – whether using a cobalt-based or an alternative drier – is currently being explored. Conceptually, the drier will be encapsulated and should protect the drier from coming into contact with the alkyd, thereby preventing the catalysis of alkyd cross-linking, hence preventing skinning and premature drying events. With this approach, the addition of an anti-skinning agent such as MEKO to the paint formulation is no longer required. In addition, facilitated by the isolation of the drier from the alkyd phase, the iron based driers may also be used as a viable substitute for the Cobalt based driers.

In conclusion, the use of MEKO may no longer be required, and the Cobalt based driers may potentially be exchanged for other drier systems (such as the iron based siccatives).

5.1 Encapsulation of the drier via encapsulation strategy I

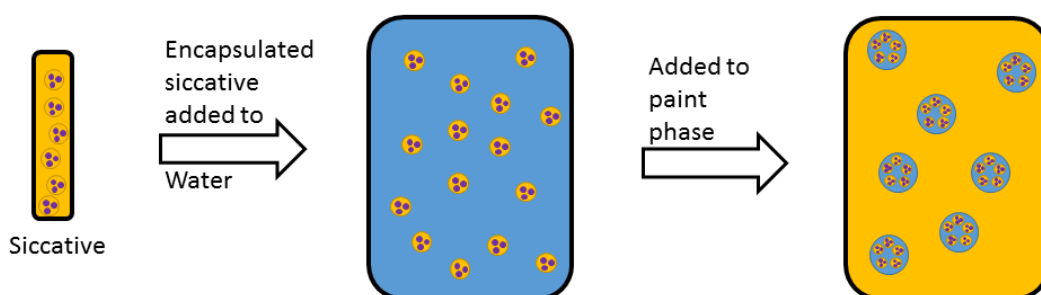


IMAGE 9

DEPICTION OF THE MODEL SYSTEM AS ENVISIONED FOR THE ENCAPSULATION OF A COBALT-SICCATIVE.

Based on the previously described studies of the water phase isolated from paint that demonstrated water domains distributed in the alkyd phase. The water domains showed size distributions in the 5 μ m-50 μ m range, making them very suitable hosts for a water dispersed encapsulation strategy. It was envisioned that encapsulation of the cobalt siccative inside core-shell system dispersed in a continuous liquid phase consisting of water (i.e. the water droplets of the paint system). This strategy should prevent undesired interactions between the siccative and the alkyd part of the paint, hence eliminate the need for addition of MEKO. Through utilization of a fragile core-shell system, application of the paint to a surface should result in enough strain that the particles break and the siccative are released resulting in a drying event.

In an initial series of experiments different conditions for the fabrication of the required core-shell particle system was investigated. In the evaluation of stability, visual confirmation by observation of phase separation events were conducted (see image Image 10 for examples of phase separation). Furthermore, the particle systems were studied with dynamic light scattering (DLS) to determine the size distribution of the formed particles. Unfortunately, none of these experiments yielded core-shell systems with the desired properties.

As a result of this, a screening of various solvent systems were conducted next (see table 8 entries 9-14). Furthermore, a stabilizing agent for improved stability was tested.

Moreover, this series of experiments were conducted in a saline water phase for the continuous water phase; the addition of a NaCl to the continuous water phase were chosen, to simulate a system resembling the complex nature of the water droplets isolated from paint samples. A NaCl concentration of 360 mg/L was found in analysed samples of the water phase isolated from a Gory88 product sample. As such, a similar concentration of NaCl was used in the advanced model system. Some of the samples from these experimental series are shown below in Image 11. Examples of phase separation can be observed.

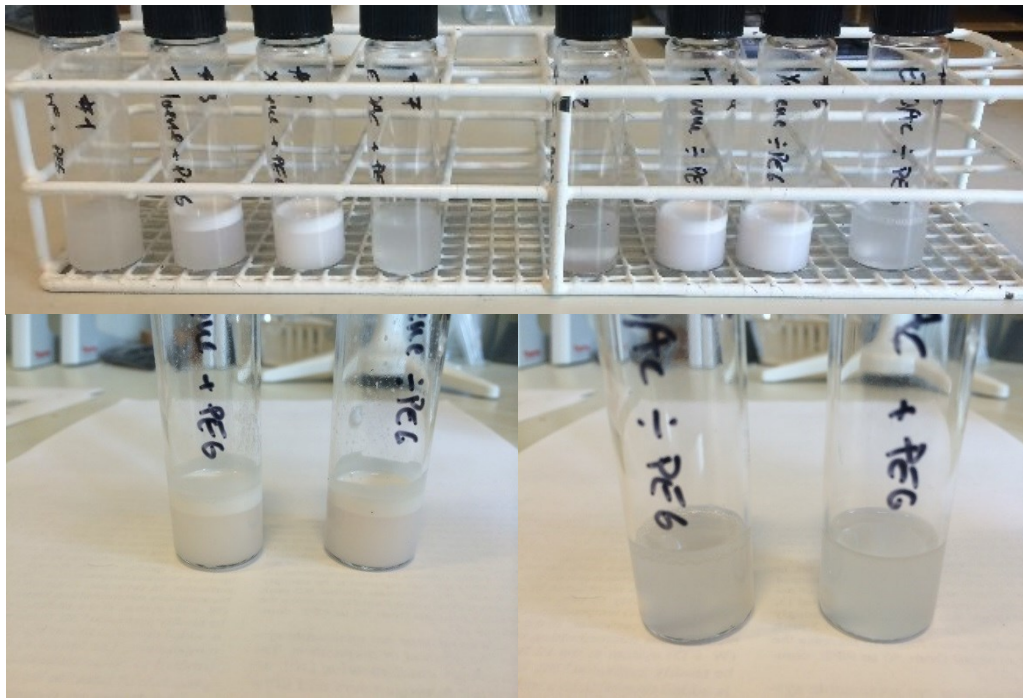


IMAGE 10
PHOTOGRAPHS OF FABRICATED FRAGILE CORE-SHELL ENCAPSULATION SYSTEMS. EXAMPLES OF PHASE SEPARATED SYSTEMS CAN BE OBSERVED

Samples containing an ether-based or acetate-based solvent as part of the solvent system combined with a stabilizing agent at 10^{w/w}% concentration of particle former showed promising stability i.e. no phase separation was observed over the course of 24 hours. Unfortunately, DLS measurement on the samples yielded data unsuitable for analysis, suggesting very broad size distributions.

TABLE 5
 VARIOUS PARAMETERS VARIED IN ATTEMPTS AT THE FORMATION OF CORE-SHELL SYSTEM FOR ENCAPSULATION OF SICCATIVES.

#	Solvent type	Water	Particle-former/ Concentration	Comment
1	Aromatic I (20 v/v%)	DI water	Particle-former I (0,7 v/v%)	Unstable – Phase separation observed
2	Aromatic I (20 v/v%)	DI water	Particle-former I (3,5 v/v%)	Short term stable (>1 hour) Phase separation observed
3	Aromatic I (20 v/v%)	DI water	Particle-former I (7 v/v%)	Short term stable (>1 hour) Phase separation observed
4	Aromatic I (2,5 v/v%)	DI water	Particle-former I (10 v/v%)	Phase stabile – DLS shows multinodal distribution
5	Aromatic I (5 v/v%)	DI water	Particle-former I (10 v/v%)	Short term stable (>1 hour) Phase separation
6	Aromatic I (10 v/v%)	DI water	Particle-former I (10 v/v%)	Short term stable (>1 hour) Phase separation
7	Aromatic I (5 v/v%)	saline water (360 mg/L NaCl)	Particle-former I (10 v/v%)	Short term stable (>1 hour) Phase separation
8	Aromatic I (10 v/v%)	saline water (360 mg/L NaCl)	Particle-former I (10 v/v%)	Short term stable (>1 hour) Phase separation
9	Alcohol I (10 v/v%)	saline water (360 mg/L NaCl)	Particle-former I (10 v/v%)	Phase stabile – DLS shows multinodal distribution
10	Acetate I (10 v/v%)	saline water (360 mg/L NaCl)	Particle-former I (10 v/v%)	Short term stable (>1 hour) Phase separation
11	Aromatic I (5 v/v%)	saline water (360 mg/L NaCl)	Particle-former I (10 v/v%) w/o stabilizing agent I	Phase separation observed – effect of stabilizing agent I uncertain
12	Aromatic II (5 v/v%)	saline water (360 mg/L NaCl)	Particle-former I (10 v/v%) w/o stabilizing agent I	Phase separation observed – effect of stabilizing agent I uncertain
13	Ether I (5 v/v%)	saline water (360 mg/L NaCl)	Particle-former I (10 v/v%) w/o stabilizing agent I	No phase separation observed – Positive effect of stabilizing agent I
14	Acetate II (5 v/v%)	saline water (360 mg/L NaCl)	Particle-former I (10 v/v%) w/o stabilizing agent I	No phase separation observed – Positive effect of stabilizing agent I

Based on the initial screening experiments, varying solvent choice and particle-former concentration, it was decided to discontinue the research efforts on core-shell strategy I as an encapsulation strategy. The instability and generally broad size distributions of the investigated particle systems were deemed incompatible with the limited size domains of the water phase observed in the final paint. Hence, further research efforts was directed at encapsulation of the siccative system by use of core-shell encapsulation strategy II.

5.2 Encapsulation of the drier via encapsulation strategy II

Encapsulation strategy II can be used to encapsulate water-soluble molecules in the core of a core-shell particle or hydrophobic molecules within the shell of such particles. Particles made by this method have radii ranging from 50 nm to a few microns, which make them an ideal candidate for siccative encapsulation in paint.

To investigate the feasibility of this strategy it was decided to utilize a two-component particle-forming system, consisting of a particle-former II and a stabilizing agent II. This system forms particles with an aqueous interior as well as an aqueous exterior, hence this system is applicable for the encapsulation of both water-soluble iron-based siccatives as well as the solvent-based cobalt siccative.

The particles were fabricated using a standard hydration technique. In a typical experiment, particle-former II, stabilizing agent II and the hydrophobic cargo was dissolved in a suitable solvent and subsequently evaporated to dryness yielding a composite thin film. The film was then re-hydrated using milliQ water (potentially containing hydrophilic cargo) during the course of several hours, followed by mild agitation for one hour to yield opaque solutions indicating successful particle formation (see Image 11 below)

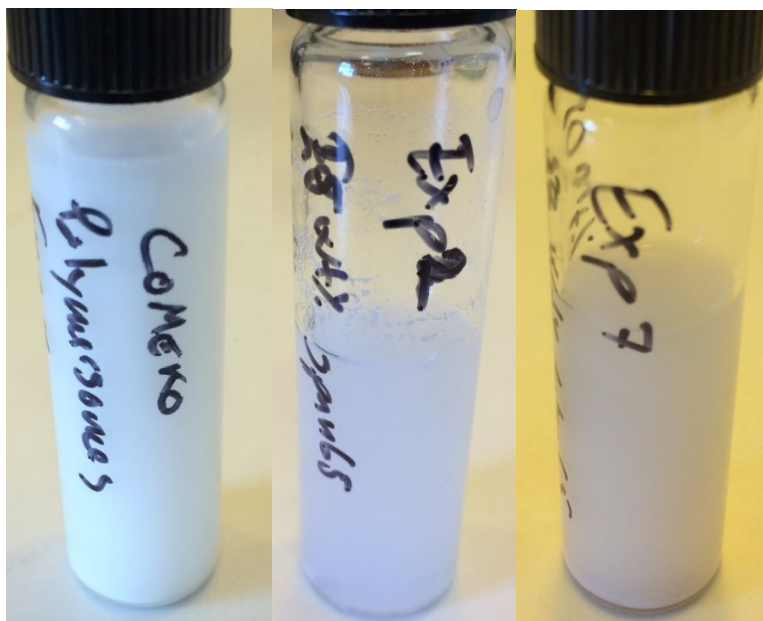


IMAGE 11
PHOTOGRAPHS OF THREE DIFFERENT SAMPLES CONTAINING PARTICLES FORMED BY ENCAPSULATION STRATEGY II. LEFT SAMPLE CONTAINS PARTICLES WITHOUT CARGO, MIDDLE SAMPLE CONTAINS 1 W/W % COBALT SICCATIVE, RIGHT SAMPLE CONTAINS 10 W/W% COBALT SICCATIVE

The generated particles were studied using DLS to gain information about size distributions, they were also observed under a light microscope to confirm the hollow nature of the particles. DLS

measurements revealed particles with diameters ranging from 20 nm to 1 micron with a multimodal size distributions. A typical plot of DLS data of the particles are shown in Image 12 below.

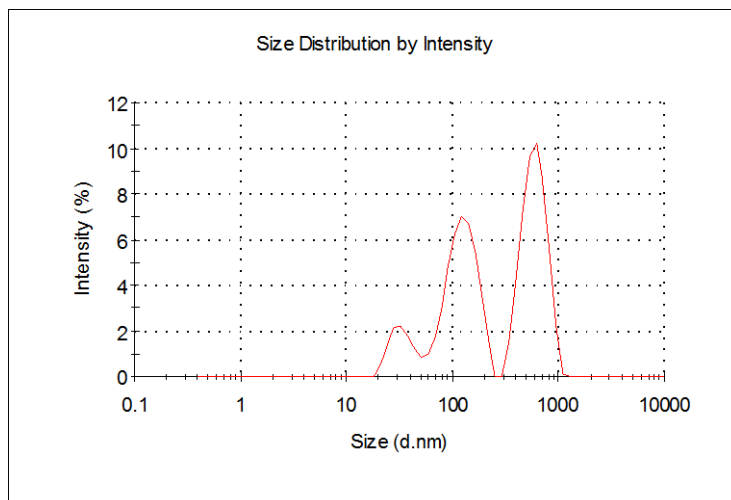


IMAGE 12
PLOT OF SIZE DISTRIBUTION DATA OBTAINED BY DLS MEASUREMENTS ON PARTICLES CONTAINING 10 W/W% COBALT SICCATIVE.

The DLS measurements confirmed the formation of particles in the typical range for such encapsulation systems. The particles were further studied under a light microscope, which confirmed that the particles obtained are hollow spheres. This is seen by focussing in different depths through the aqueous sample containing particles, whereby gray spheres, corresponding to the shell of the particles, and dark circles corresponds to the shell around the hollow core (white interior) can be observed (see image below).

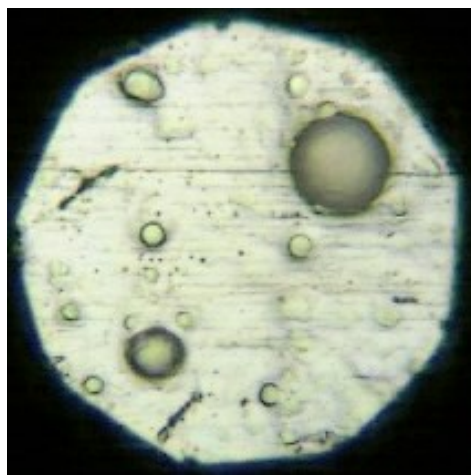


IMAGE 13
PHOTOGRAPHS OF PARTICLES FABRICATED IN PRESENCE OF A WATER-BASED IRON SICCATIVE TAKEN UNDER MICROSCOPE AT 50X MAGNIFICATION. THE PARTICLES HAVE SIZES RANGING FROM 20 NANOMETER TO 1 MICROMETER

Based on the positive results obtained on the core-shell particle preparation by standard hydration, a series of particles loaded with a cobalt complex or cobalt siccative was prepared and analyzed by DLS and light microscopy followed by raman spectroscopy. Raman spectroscopy was utilized to

confirm that the cobalt cargo i.e. cobalt complex or cobalt siccative, was present in the particles. See Image 14 below for examples of raman spectra of particles without cargo, particles with cobalt cargo plotted with a reference raman spectra of the pure cobalt cargo.

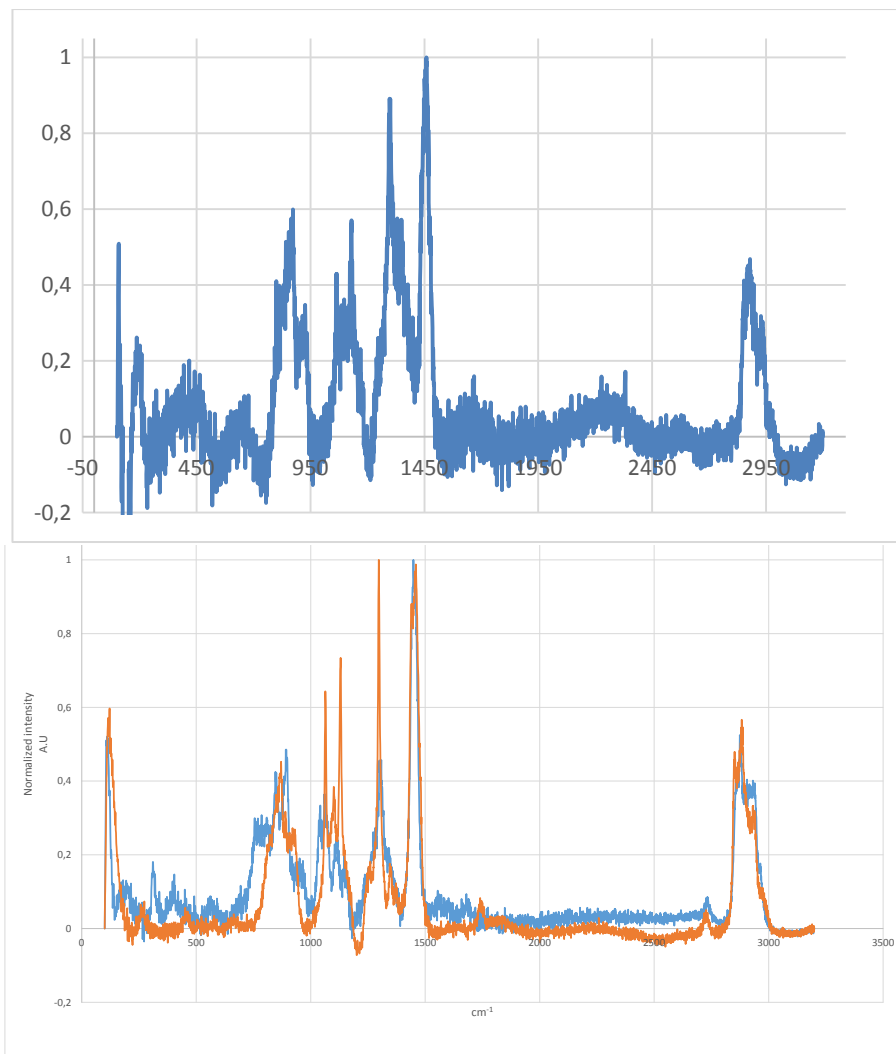


IMAGE 14

RAMAN SPECTRA FOR THE PARTICLES. TOP SPECTRA: PARTICLES WITHOUT CARGO. BOTTOM SPECTRA: PARTICLES CONTAINING COBALT COMPLEX PLOTTET WITH REFERENCE SPECTRA OF THE PURE COBALT COMPLEX

The raman spectra of the particles containing a model cobalt cargo (cobalt II ethylhexanoate) shows peaks in good agreement with the reference spectra strongly supporting that the cobalt cargo is indeed captured in the particles. Investigations of particles loaded with an iron-based siccative are currently on-going as the water-soluble nature of the siccative complicates purification of the core-shell particles. Based on these very positive preliminary results, tests of the core-shell-encapsulated siccatives added to the paint formulation were conducted. A series of core-shell encapsulated siccatives, both Fe- and Co-based, were prepared with increasing siccative content ranging from 50% to 100%. Moreover, these core-shell particles were synthesized by an expanded approach employing a purification strategy after the initial formation conditions. This advanced procedure was employed to ensure that any “free” siccative would be minimized and was realized utilizing several washing steps.

TABLE 6:
CARGO AND LOAD FOR CORE-SHELL ENCAPSULATION OF SICCATIVES.

#	Cargo	Amount	Theoretical load
1	Fe	0.5 mL	50 w/w%
2	Fe	1 mL	100 w/w%
3	Fe	2.5 mL	250 w/w%
4	Fe	5.0 mL	500 w/w%
5	Fe	7.5 mL	750 w/w%
6	Fe	10 mL	1000 w/w%
7	Fe	0 mL	Control
8	Co	0.5 mL	50 w/w%
9	Co	1 mL	100 w/w%
10	Co	2.5 mL	250 w/w%
11	Co	5.0 mL	500 w/w%
12	Co	7.5 mL	750 w/w%
13	Co	10 mL	1000 w/w%
14	Co	0 mL	Control

The purified siccative-loaded core-shell particles were subsequently added to wood-protecting paint void of siccative and water supplied by PPG. The suspended particles were added in amounts corresponding to the water content of Gory 88. This allowed for the fabrication of a series of paint samples containing varying amount of encapsulated siccative. Two different series were prepared by this strategy, one containing a cobalt siccative and one containing a water-soluble iron siccative. The samples were evaluated at PPG for undesired premature drying events as well as tested in drying experiments to determine if drying-function is retained for the encapsulated siccative. In general samples containing very high siccative loadings i.e. 750-1000 w/w% resulted in premature drying events, most likely due to insufficient encapsulation as a result of overloading (see Image 15 below).



IMAGE 15
 PHOTOGRAPHS OF CORE-SHELL ENCAPSULATED SICCATIVES IN WOOD-PROTECTING PAINTS. UNDESIRABLE DRYING EVENTS ARE OBSERVED FOR HIGHER LOAD LEVELS OF SICCATIVE (SAMPLES TO THE RIGHT). THE CHANGE IN COLOR IS SPECULATED TO RESULT FROM OXIDATION OF THE COBALT SICCATIVE.

For further evaluation of the remaining samples loaded with encapsulated Fe-complex siccative, a Drying recorder was used (see Image 16).

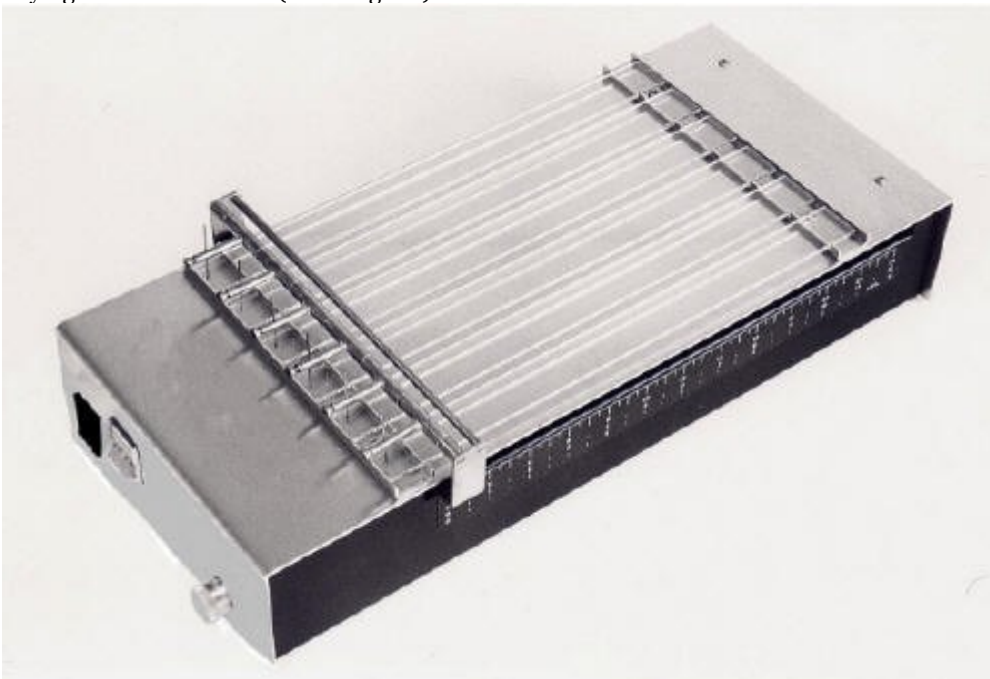


IMAGE 16
 DRYING RECORDER USED AT PPG TO EVALUATE DEVELOPED SICCATIVE ENCAPSULATION

In the drying recorder, the drying time is measured by allowing a needle to scratch a film applied on a specific glass plate. The scratching is a very slow process and the speed of scratching can be chosen to be either 1 cm per hour (24 hours measurement) or 0,5 cm per hour (48 hours measurement). In general, samples that never dries leave no traces since the film will melt together just after the needle has passed by. Similar activity appear in the initial drying phase during the evaporation of the solvent for drying systems. Film that dries fast will in general give traces during

the curing regime and after fully dry the needle will only scratch on top of the surfaces leave signs of scratches out. Four different stages of drying is defined by this technique and depending on film thickness and coating those stages are more or less pronounced.

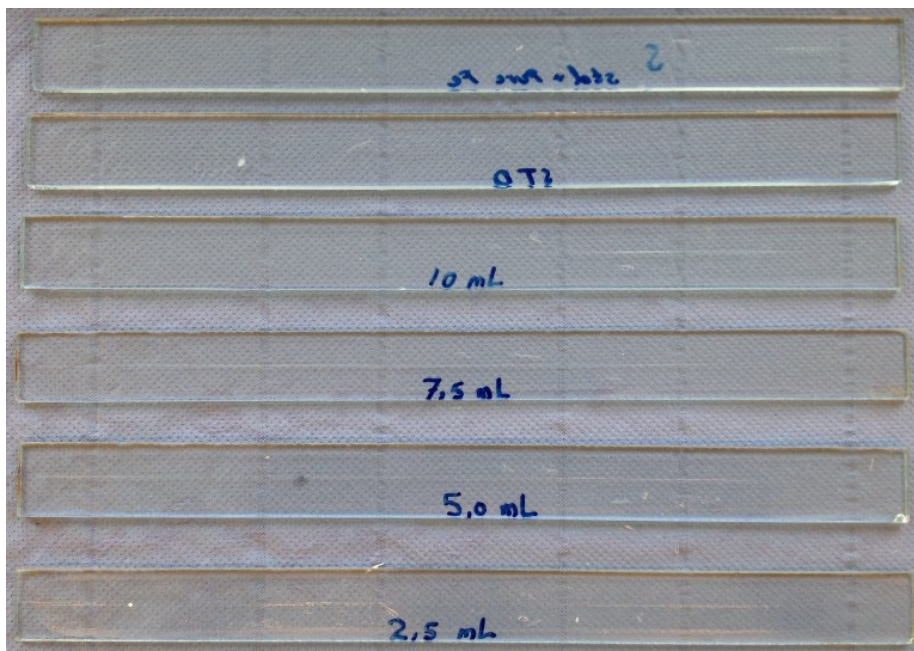


IMAGE 17
6 SAMPLES WAS TESTED USING THE DRYING RECORDER, THESE WERE SAMPLES 3-6 FROM TABLE 6 ALONG WITH TWO REFERENCE SAMPLES, ONE WITH NO SICCATIVE AND ONE WITH THE STANDARD SICCATIVE SYSTEM.

After an initial screening, six samples where chosen for tests on the drying recorder, these six where four Fe-complex containing samples (samples 3-6 in Table 6), reference sample with no siccative, and a standard sample with the normal siccative system from PPG (Image 17). Samples 5 and 6 (750 w/w% and 1000 w/w%) reveal decent drying properties, though less performance than standard, but the absence of anti-skinning (MEKO) in the can revealed skin formation. The reference with no siccative reveal very long drying and after 48 hours there was still no sign of drying (as expected). Using lower amount of dryers (such as sample 3, 250 w/w%) were not efficient enough, though drying was observed. Although, at this low amount of dryers and low drying performances, skin formation was observed in the can, but the effect was only observed after a couple of weeks.

It seems like drying is obtained when loaded with the encapsulated drying technology, but not without creating film formation in can. The magnitude of film formation in the can seems to relate directly to the amount of encapsulated dryer incorporated in the matrix. In the laboratory samples with encapsulated dryer suspended in water, the material seems to be very stable, and the capsules are intact more than six month after synthesis. This leads to the belief, that the encapsulation technology is a viable route to avoiding the use of Co(II) complexes and MEKO in the wood protection products. However, the stability of the capsules are currently not good enough when mixed into the very complex paint mixture, and they either leek the dryer into the paint, or they collapse over time, thus releasing the dryer into the paint matrix causing film formation.

5.3 Encapsulation of the drier via encapsulation strategy III

In light of the poor performance of siccative encapsulation strategy II, it was decided by PPG and DTI to attempt encapsulation by a third strategy relying on similar principles as previous investigated strategies with further compartmentalization of the core-shell system in a onion structured multi-lamellar structure. It is envisioned, that further compartmentalization can enable better encapsulation properties combined with the desired release profile.

In a typical experiment, a particle-forming agent III in a suitable solvent was subjected to a series of heating and cooling events followed by mechanical activation to synthesize compartmentalized core-shell particles in which water-soluble cargo can be loaded.

The obtained solutions were characterized by microscopy (see Image 18). Several structural elements ranging in size from 2-20 microns were observed. Furthermore, particles with features resembling what would be expected for compartmentalized particles were observed. Unfortunately, time-constraints did not allow fabrication of a large enough sample set to confirm with scientific certainty, that the desired compartmentalized particles form under the utilized conditions.

Moreover, further experiments are required to demonstrate the feasibility of this encapsulation strategy for applications in a paint matrix.

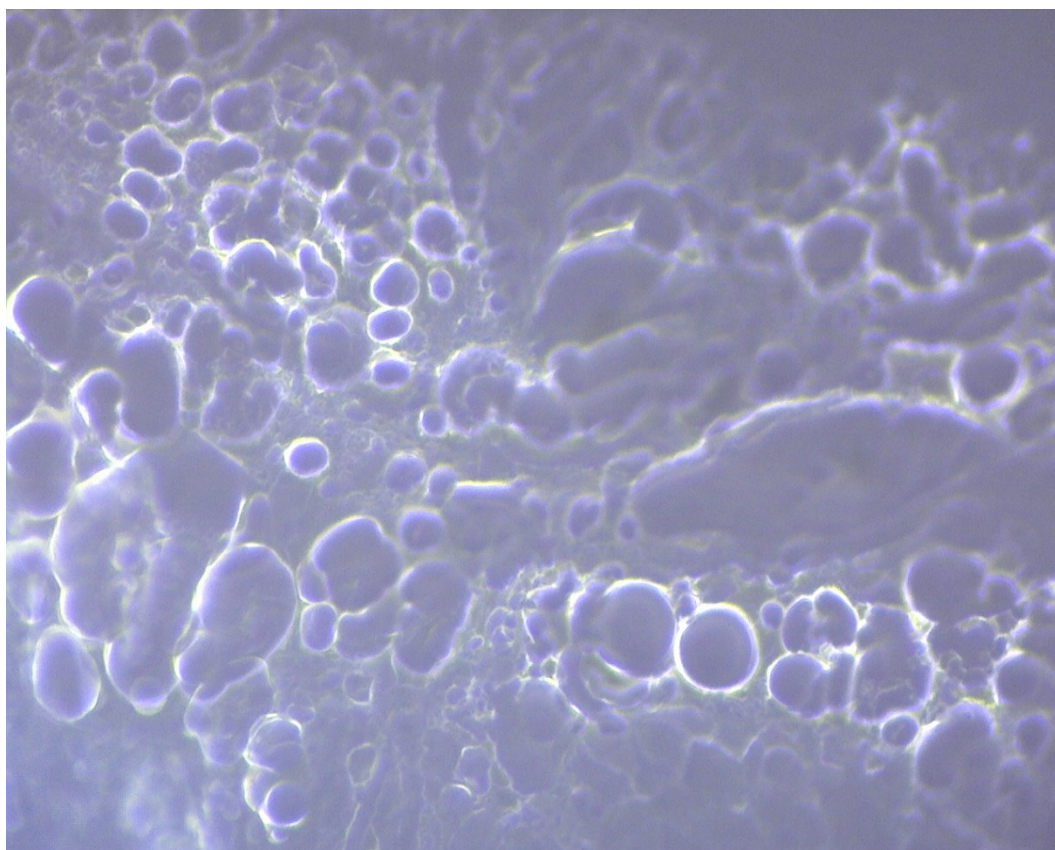


IMAGE 18

PHOTOGRAPHS OF COMPARTMENTALIZED CORE-SHELL PARTICLES USING LIGHT MICROSCOPY AT 800X MAGNIFICATION. SPHERICAL PARTICLES OF VARYING SIZE ARE OBSERVED. HOWEVER, THE COMPARTMENTALIZED FEATURE OF THESE PARTICLES CAN NOT BEEN CONFIRMED.

In conclusion, three different strategies for the encapsulating of siccatives for paint applications have been investigated. Strategies II and III show great promise but each with their own challenges. The stability of system II in the finished paint matrix is currently not good enough, a part of this is contributed to the very complex surfactant system found in these wood protection mixtures, all of which is not fully understood, or even known.

For strategy III the system is further stabilized via a further compartmentalization of the encapsulation system. This system is foreseen to show much more stability in the final mixtures, but a major challenge is the use of very expensive starting materials; therefore, further study is needed both in the stabilities of the model system, but also in the development and/or selection/testing of cheaper starting materials.

References

- Bieleman, J., Ed. (2000). Additives for Coatings. Additives for Coatings.
- de Boer, J. W., P. V. Wesenhagen, et al. (2013). "The Quest for Cobalt-Free Alkyd Paint Driers." European Journal of Inorganic Chemistry **2013**(21): 3581-3591.
- Discher, B. M., H. Bermudez, et al. (2002). "Cross-linked Polymersome Membranes: Vesicles with Broadly Adjustable Properties." The Journal of Physical Chemistry B **106**(11): 2848-2854.
- Larsen, J. K. and E. Wallström (2006). "Substitution of cobalt driers in wood coatings." Working Report, Danish EPA **20**.
- Lee, J. C., H. Bermudez, et al. (2001). "Preparation, stability, and in vitro performance of vesicles made with diblock copolymers." Biotechnol Bioeng **73**(2): 135-45.
- Mayer, L. D., M. J. Hope, et al. (1986). "Vesicles of variable sizes produced by a rapid extrusion procedure." Biochim Biophys Acta **858**(1): 161-8.
- Miccicha, F., E. Oostveen, et al. (2005). "The combination of reducing agents/iron as environmentally friendlier alternatives for Co-based driers in the drying of alkyd paints." Progress in Organic Coatings **53**(2): 99-105.
- Paleos, C. M., D. Tsiourvas, et al. (2011). "Preparation of Multicompartment Lipid-Based Systems Based on Vesicle Interactions." Langmuir **28**(5): 2337-2346.
- Pilemand, C., E. Wallström, et al. (2003). "Substitution of Cobalt Driers and Methyl Ethyl Ketoxime." Environmental Project, Danish EPA **884**.
- Rodriguez-Garcia, R., M. Mell, et al. (2011). "Polymersomes: smart vesicles of tunable rigidity and permeability." Soft Matter **7**(4): 1532-1542.
- San, L. Y. and A. Gabrielle (2013). MEKO Alternatives - Literature review, internal document, PPG Europe BV.
- Soucek, M. D., T. Khattab, et al. (2012). "Review of autoxidation and driers." Progress in Organic Coatings **73**(4): 435-454.
- Tanase, S., J.-C. Hierso, et al. (2003). "New insights on the anti-skinning effect of methyl ethyl ketoxime in alkyd paints." New Journal of Chemistry **27**(5): 854-859.
- Van Gorkum, R. and E. Bouwman (2005). "The oxidative drying of alkyd paint catalysed by metal complexes." Coordination Chemistry Reviews **249**(17): 1709-1728.

Appendix 1: Abbreviations

MEKO	Methyl ethyl ketoxime or 2-butanone oxime
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
SVHC	Substances of Very High Concern
VOC	Volatile organic compounds

CoMEKO – Substitution of cobalt in wood protection products

The aim of this project was to substitute harmful cobalt (II) siccatives as well as the anti-skinning agent methyl ethyl ketone (MEKO) from alkyd wood protection products. This was approached using unconventional technologies while maintaining focus on the overall properties of the final product, such as appropriate drying times and storage stability were maintained or improved. The alternative approaches should create fewer concerns regarding human health as well as the environment compared to the substituted compounds.

This project was divided into a) design of the siccative system and method development, b) Experiments on model systems and c) formulation and test of the wood protection systems. During the course of this project, a number of possible routes to reduction and/or elimination of the use of the Cobalt(II) and MEKO siccative system for wood protection products have been identified. Many of these involve a change in the physical handling of the paint products, avoiding activation of the dryer system prior to opening and use of the paint. Common for many of these solutions are that long-time storage after opening is no longer an option, as the stability of the system is hampered by exposure to oxygen, or a post-activation step. However systems including three new encapsulation strategies to selectively release the dryer system upon application of the paint systems showed promising results, although it was not possible to make a fully stable system within the timeframe of this project. The encapsulation technology could be a viable route to avoiding the use of Co(II) complexes and MEKO in the wood protection products. Further investigations are needed in order to reach systems that can be implemented in wood protection products.

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