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A NEW CURE
FOR PAINT
FORMULATORS**

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SYNTHESISING A NEW CURE FOR PAINT FORMULATORS

High-solids alkyd-resin coatings with cobalt-free and MEKO-free components. By Dr Claude Nootens, Luer Chem.

Formulators face drying and hardness challenges with high-solids alkyd resins, which this research seeks to resolve. Using an alternative drier and anti-skinning agent to comply with regulations can negatively impact a coating's drying properties. However, researchers have found a promising combination for successful curing and hardness development.

The paint industry is constantly facing new challenges. Nowadays, in addition to the stringent rules and regulations regarding VOC for architectural and industrial maintenance coatings, new trends such as sustainability are becoming increasingly important. This can be an opportunity to reconsider resins based on natural feedstock such as alkyd resins, which are based on seed oil. VOC regulations have resulted in the development of water-borne alkyd coatings in place of solvent-borne alkyd coatings. However, the resulting paint performance does not always meet the requirements for the highest-end market segment (e.g. metal protection). In response to this, the industry has developed high solids solvent-borne alkyd coatings. High solids alkyd resins can be made by preparing lower viscosity long oil alkyd resins. Such resins are prepared by lowering their molecular weight, using highly functional polyols. However, first reducing the molecular weight of the alkyd resin can have a significant negative

effect on drying time and hardness of the resulting coating. Secondly, the use of certain highly functional polyols can induce gelation during the preparation of the alkyd resin and will often necessitate a chain stopper such as benzoic acid to reduce the risk of gelation.

On the other hand, when using a resinous polyol such as styrene allyl alcohol copolymer, there is no need to use a chain stopper. One explanation could be that there is a steric hinderance effect of the aromatic ring in this copolymer which prevents some hydroxyl groups from easily reacting.

Styrene allyl alcohol copolymer is a hard, low molecular weight resinous polyol containing primary hydroxyl and aromatic structures. The styrene allyl alcohol copolymer is produced by radical polymerisation of styrene and allyl alcohol monomers [1, 2] (*Figure 1*).

It has been reported that using styrene allyl alcohol (SAA) copolymer as partial replacement of pentaerythritol and phthalic anhydride reduces the molecular weight (Mw) of a long oil alkyd resin without having a significant impact on the molecular weight in number (Mn) [3]. The reduction of the polydispersity (Mw/Mn) allows to reduce the alkyd resin viscosity significantly without strongly negatively affecting the coating performance. Therefore, styrene allyl alcohol-modified alkyd resins can be formulated at high or very high solids content while maintaining appropriate handling viscosity.

RESULTS AT A GLANCE

- In addition to stringent VOC regulations, the paint industry faces additional restrictions on the type of drier and anti-skinning agent, which can be used in oxidative air-drying alkyd coatings.
- In response to these challenges, we studied the drying evolution with two cobalt-free driers and a methyl ethyl ketoxime (MEKO)-free anti-skinning agent.
- Combining a manganese-based drier with a MEKO-free anti-skinning agent proved promising and an optimal level was determined.
- A styrene allyl alcohol copolymer was used to prepare a high solids alkyd resin, which is characterised by low viscosity.
- Successful curing with a cobalt-free drier in the presence of a MEKO-free anti-skinning agent presents alternatives for formulators that comply with increasing regulation.

Table 1: Typical properties of the styrene allyl alcohol copolymer used.

Typical properties	SAA
Number average molecular weight (Mn) by GPC	1,500
Weight average molecular weight (Mw) by GPC	3,000
Hydroxyl number (mg KOH/g)	210
Hydroxyl content, wt%	6.4
Equivalent weight	267
Glass transition temperature (Tg), °C	62
APHA colour (30 % in MEK)	40
Specific gravity	1.05

ALTERNATIVES TO INGREDIENTS OF CONCERN IMPACT DRYING PROPERTIES

Nowadays, in addition to the VOC restriction that impacts solvent-borne alkyd-based coatings, there are other ingredients of concern that are usually present in the coating formulation. Firstly, cobalt driers have been identified by the European Union as having high toxicological potential which has created a market need to formulate with a cobalt-free alternative. Secondly, the European Commission published the classification of methyl ethyl ketoxime (MEKO) as a 1B carcinogen with a concentration limit at $\geq 0.1\%$ (ATP 15 Part 3 Annex VI). From 1 March, 2022, formulators cannot use MEKO if it meets or exceeds the concentration limits. This directive, coupled with the many protocols required for handling the raw material based on its hazard pictograms, is a

Figure 1: Synthesis of styrene allyl alcohol copolymer.

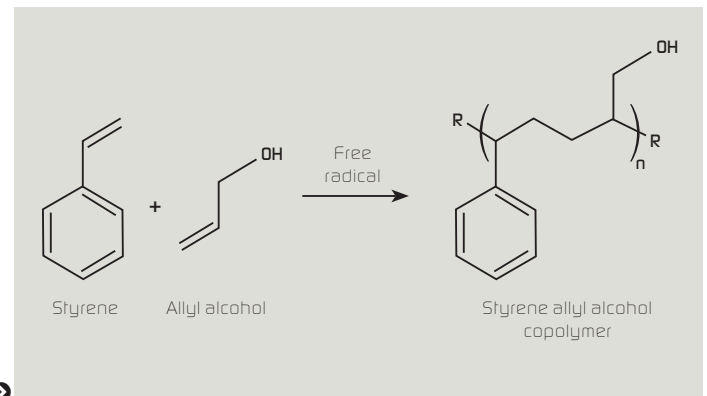


Table 2: Drying recorder results obtained for comparative testing.

Alkyd resin	Drier	Anti-skinning agent	Stage 2 (hrs)	Stage 3 (hrs)	Stage 4 (hrs)
Reference	Mn	SH	2.1	4.5	8.3
SAA	Mn	SH	2.5	2.7	9.0
Reference	Fe	AS	2.3	9.0	12.0
SAA	Fe	AS	3.4	3.7	15.2

Table 3: Summary of drying recorder results for the SAA-based resin.

Mn drier (% Wt of resin solids)	Anti-skinning agent (% Wt on total)	Stage 2 (hrs)	Stage 3 (hrs)	Stage 4 (hrs)	Time to skinning (days)
0.5	0	4.8	7.8	23.0	10
0.5	1.1	4.6	7.0	14.3	10
1.8	1.5	2.5	2.7	9.0	> 14
1.8	0.7	2.3	2.4	8.9	6
3.0	0	0.9	1.2	10.3	1

significant regulatory push to remove this raw material from alkyd formulations.

The use of an alternative drier and anti-skinning agent will impact the coating's drying properties and therefore require a reformulation of the coating.

For this study, we first prepared a long oil high solids alkyd resin using a styrene allyl alcohol copolymer as a resinous polyol. This styrene allyl alcohol copolymer has a composition (expressed in mole) of 70 % of styrene and 30 % of allyl alcohol. *Table 1* reports the typical properties of this styrene allyl alcohol copolymer.

Secondly, we studied the oxidative air-drying (curing) of this SAA-based alkyd resin using different combinations of drier/anti-skinning agent that comply with the new market requirements (cobalt-free and MEKO-free). The selection of these ingredients and the optimisation of their concentrations related to the curing time using a drying recorder. We also measured the coating hardness as a function of the drying time.

EXPERIMENTAL

The preparation of alkyd resins is well-known in the art. Although the amounts of ingredients (seed oil, polyol and anhydride) are reported,

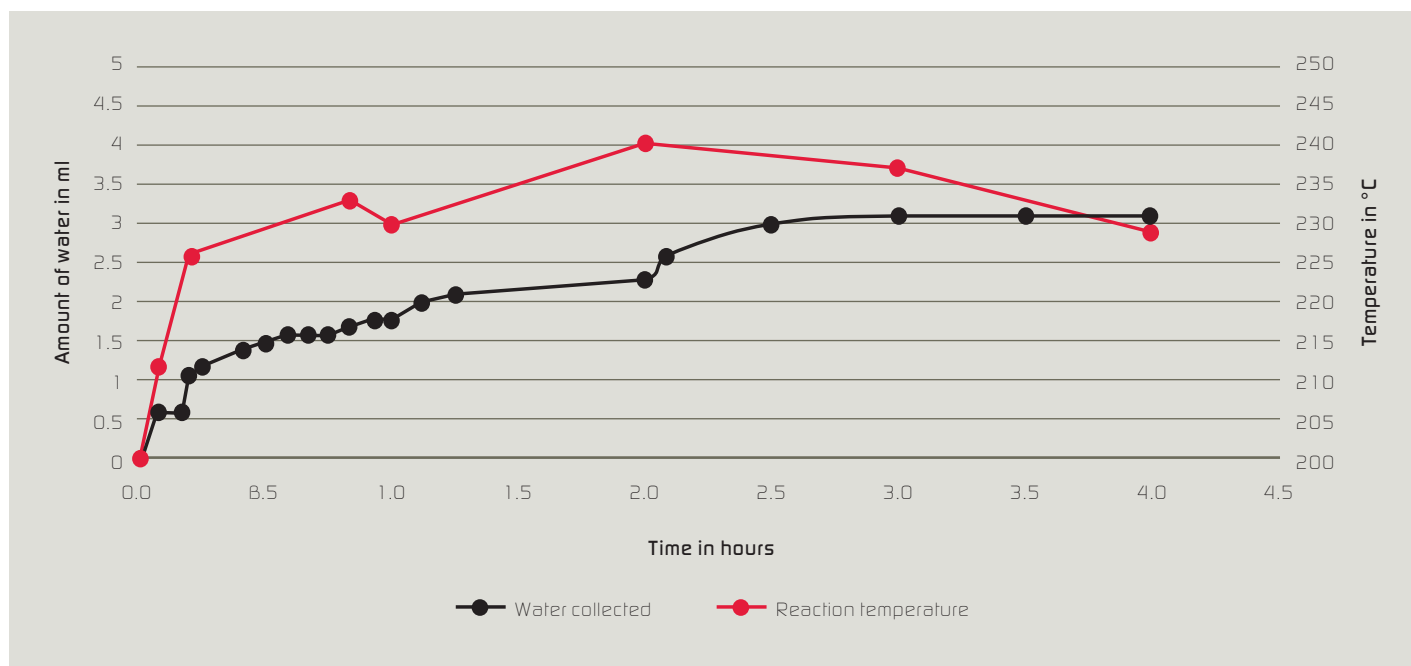
the level of solvent (xylene) used to remove water by azeotropic distillation is rarely mentioned. This is an important consideration to avoid unwanted side reactions when preparing the alkyd resin, and particularly in the case of high solids alkyd resin.

We used the standard two-stage process to prepare the alkyd resin. Soybean oil was used as the seed oil with pentaerythritol and phthalic anhydride. In addition, styrene allyl alcohol copolymer was used as a resinous polyol at 5 % weight based on the solids content of the resin. This composition constitutes a starting point and could be further optimised, especially regarding the amount of pentaerythritol and phthalic anhydride used.

The detailed recipe used for the preparation of the high solids long oil alkyd resin is reported below:

Stage 1 - Alcoholysis: Soybean oil (61.6 g), pentaerythritol (13.3 g), styrene allyl alcohol (5 g) and dibutyl tin oxide (0.05 g) were charged to a 250 ml 3-necked round-bottomed flask equipped with a Dean Stark trap and condenser, a nitrogen supply and a thermometer inlet adaptor. The main neck of the flask was left free of attachments to allow sampling of the reaction. The equipment was flushed with nitrogen for 5 minutes and then the reaction mixture was heated to 250 °C

Figure 2: Evolution of water collected and reaction temperature.



with magnetic stirring at 1500 rpm (set temperature 270 °C of the block heating equipment). The reaction was allowed to proceed for 30-60 mins after reaching a heating block temperature of 250 °C. The first stage of the reaction was concluded when a sample of the reaction mixture was soluble in a 1:1 mixture with hot methanol.

Stage 2 – Polymerisation: The reaction mixture was allowed to cool to 180 °C (hotplate lowered, approximately 10 minutes), then the trap was partly loaded with xylene (11 ml). Phthalic anhydride (22.9 g) and xylene (15 g) were added to the reaction mixture. The hotplate was returned to position to recommence heating and the set temperature was increased to 310 °C. The start of reaction time was taken as the first drops of distillate passing over to the trap (reaction temperature ~230 °C at this point). The reaction was allowed to proceed for 4-6 hours, with monitoring of reaction temperature throughout (reached 250 °C after ~1 hour and remained at 250-260 °C after that time). The measurement of acid content commenced after 4 hours. We used aluminium foil lagging around the distillation path and reaction flask to reduce heat loss and maintain the reaction temperature.

The reaction was considered finished once an acid content <10 mg KOH/g was achieved. On conclusion of the reaction, it was allowed to cool to 170-180 °C and white spirit (33 g) was added.

The amount of water collected, and the reaction temperature of resin were regularly monitored throughout the reaction: *Figure 2* shows the results of that monitoring during the polymerisation stage of the reaction. After 3 hours, no increase in the amount of water collected was observed, indicating that the reaction was likely to be mostly complete at that point. It is also possible to see that the reaction temperature decreases towards the end of the reaction, while the set temperature of the hotplate was not reduced.

It was observed that four hours were sufficient to achieve the targeted acid value for the resin described above.

The non-volatile content of the resulting resin solution was determined by heating the resin solution (~1 g) for 1 hour at 120 °C, to allow calculation of the resin acid content according to ASTM D1639. The resulting SAA-based alkyd resin has a measured solids content of 74 % after adding white spirit, which means that only ~2 g xylene is left in the resin at the end of the reaction. The remaining xylene (~13 g) was transferred to the Dean Stark. The acid value of the alkyd resin is 1.5 mg KOH/g solids resin.

COMPLIANT NON-PIGMENTED COATING FORMULATION

The next part of this study concerns the development of a non-pigmented coating formulation which complies with new market requirements in terms of drier and anti-skinning agent (cobalt-free and MEKO-free).

A quick screening was first carried out to select a commercial alternative drier and anti-skinning agent. For this, the drying evolution of the clear coat was studied for two driers (one based on manganese, and one based on iron), each of them with a different MEKO-free anti-skinning agent. Their levels were set-up at the mid-point of their recommended value, respectively 1.8 % on solids resin and 1.5 % on total formulation. The SAA-based alkyd resin was compared to a lab-made alkyd resin which did not contain SAA. This alkyd resin, which was used as reference, had a very high viscosity and therefore the total solids content for the clear coat formulations was set to only 65 % to avoid viscosity handling issues with the reference alkyd resin. In addition, the clear coat formulation contained a polyether modified polydimethylsiloxane, as a wetting agent additive.

Drying time of the alkyd resin-based coatings was measured using a drying recorder according to ISO 9117-4. A 100 µm wet coating film was applied to a glass plate and immediately a stylus was commenced to be pulled through the coating over a period of 24 hours.

The various stages of drying were determined from the appearance of the track marked in the coating by the stylus. The different stages are represented in *Figure 3* and can be described in stages: Stage 1 = start point of test, Stage 2 = set to touch time, Stage 3 = tack-free time, Stage 4 = hard-dry time and Stage 5 = through-dry time.

The results presented in *Table 2* show that the manganese-based drier is more efficient for faster ambient curing of the alkyd resins (stages 3 and 4), as expected, based on current knowledge.

Therefore, we selected the Mn drier/SH anti-skinning agent combination to further study the clear coat composition.

OPTIMUM ADDITIVE RATIO ESTABLISHED

In the next part of the study, using a Design of Experiment (DoE), the SAA-based alkyd resin was formulated with different amounts of the manganese-based drier and anti-skinning agent SH.

In this way, the impact of their respective levels on the drying behaviour can be studied and their optimum level can be determined. *Table 3* presents the data for the SAA-based alkyd resin.

These data show that the mid-point of the recommendation for the Mn drier and anti-skinning agent SH, respectively 1.8 % of solids resin and 1.5 % of total formulation, is close to optimum. Significantly lowering the amount of Mn drier has a negative impact on the drying evolution, whereas significantly increasing this amount does not really affect the drying evolution. One can see that the amount of anti-skinning agent used in the screening work is also close to optimum. Based on these data from the DoE study, the final level of Mn drier was set at 1.6 % solids resin and for 1.6 % anti-skinning agent based on the total coat formulation.

The final non-pigmented coating composition is reported in *Table 4* and will be used for the study of coating hardness development.

FURTHER OPTIMISATION OF HARDNESS POSSIBLE

The coatings were applied on duplicate, solvent wiped, glass plates using an 80 µm wire-wound bar applicator and allowed to dry/condition at 23 °C/50 % relative humidity.

The coating hardness was measured as König pendulum hardness according to ISO 1522:2006. The hardness of each coating was tested after 3 days, 7 days and 14 days.

On completion of testing, the dry film thickness of the coatings was measured by difference using a set of callipers. The film thickness and hardness data are reported in *Table 5*.

The SAA-based alkyd resin has a slightly lower hardness compared to the reference. This observation may result from the lower average molecular weight of the SAA-based alkyd resin and by the fact that the SAA-based alkyd resin was prepared at a higher alcohol-to-acid ratio than the standard long oil alkyd (1.2 instead of 1.15).

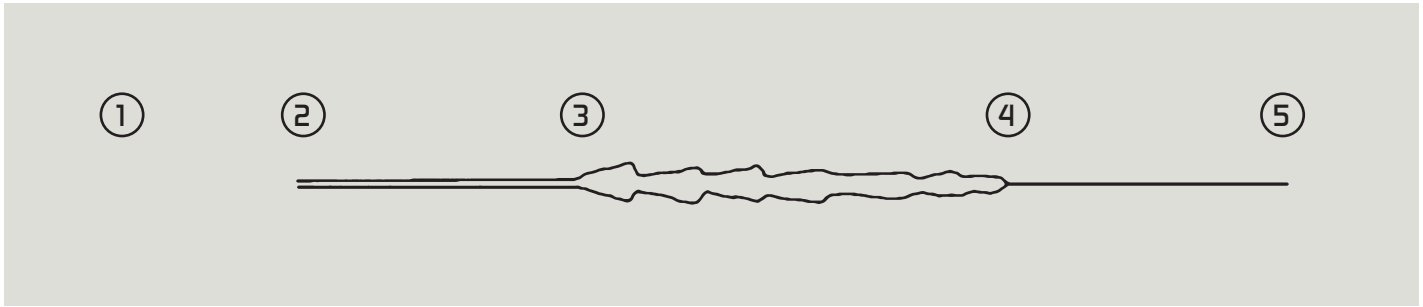
It is expected that modifying the stoichiometry would allow further optimisation of the SAA-based alkyd resin.

The viscosity of the reference alkyd resin is very high, which severely limits its formulation at high solids content for practical handling reasons. However, the SAA-based alkyd resin has such a low viscosity that it can be formulated at a very high solids content.

USEFUL COMBINATION FOR HIGH SOLIDS ALKYD RESINS

Thanks to the ability to control an adequate level of solvent (xylene) present in the reactor, it was possible to successfully prepare a long oil alkyd resin with a very low acid value, using a styrene allyl alcohol copolymer. The SAA-based alkyd resin is characterised by low viscosity and therefore such resin can be formulated at high solids content. The study of the oxidative air-drying (curing) of the alkyd resin with a commercial cobalt-free drier and MEKO-free anti-skinning agent dem-

► Figure 3: Stages of coating drying as they appear during drying recorder testing.



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onstrates that the combination of a manganese based drier with a specific MEKO-free anti-skinning agent coded SH can be used for the oxidative air-drying of high solids long oil alkyd resins. The use of styrene allyl alcohol copolymer as a resinous polyol has demonstrated its potential in formulating high solids alkyd resins. ◀

ACKNOWLEDGEMENTS

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Table 4: Final clear coat formulation.

	Reference	SAA
Alkyd resin (g)	18.0 (69% S.C.)	18.0 (74% S.C.)
White spirit additional (g)	0.7	2.0
Mn drier (g)	0.2	0.21
SH anti-skinning agent (g)	0.3	0.32
Wetting additive (g)	0.05	0.05
Formulation solids content (%)	64.8	65.0

Table 5: Film thickness and König pendulum hardness.

Alkyd resin	Film thickness (µm)	Hardness, 3 days (s)	Hardness, 7 days (s)	Hardness, 14 days (s)
Reference	70	14.2 ± 0.7	16.2 ± 0.5	15.9 ± 0.4
SAA	50	13.0 ± 0.2	14.0 ± 0.2	14.4 ± 0.5