



QUICKER CROSSLINKING

Built-in reactivity is the key to better curing of 2K PU coatings. By Jan Klesing, Thomas Krey and Carolin Wallenhorst, ASK Chemicals GmbH.

Water-based 2K PU paints suffer from slow flash-off and curing times. A new water-borne polyester polyol with higher cross-linking density and isocyanate reactivity was developed. Significant reductions in drying time and initial hardness development were obtained while maintaining all final properties.

Since the discovery of the polyaddition of diols and diisocyanates by Otto Bayer at the end of the 1930s [1], polyurethane resins have continued to develop and today are indispensable as high-quality coating components for furniture, vehicle and industrial paints. A major reason for this is their excellent mechanical properties paired with high chemical resistance and, in many cases, outstanding weather resistance [2]. Over time, a great deal of development work has been invested in polyols as well as in the hardener component, and today the polyol types available on the market are much more strongly represented than alternative isocyanate hardeners. This broad range of polyol types thus meets different property profiles, which are used in the most varied applications.

DESIGNING OUT SLOW DRYING IN WATER-BORNE PUS

For decades, water-borne 2K PU coatings have been gaining market share and replacing solvent-borne alternatives with success. In general, water- and solvent-borne 2K PU coatings show comparable properties in terms of high gloss and final hardness as well as excellent

scratch and chemical resistance.

However, one drawback of water-borne systems is related to their low curing speed compared to solvent-borne alternatives. This limitation in performance is mainly driven by the poor selection of suitable catalysts, which also promote side reactions in aqueous media.

A water-emulsifiable polyester polyol backbone with catalytically active building blocks was developed to improve this situation. The polyester polyol emulsion exhibits a pronounced degree of branching as well as a high affinity for isocyanates. Aqueous 2K PU coatings made from this show a significantly improved drying speed while maintaining very high gloss, weather and colour stability as well as excellent hardness.

REGULATORY AND PERFORMANCE DEMANDS ON POLYOLS

In order to meet the ever stricter VOC regulations of the European Union and more recently those in the People's Republic of China, two different approaches have become established: high-solids and water-emulsifiable polyols. High-solids polyols are a class with a low molecular weight and relatively low amount of solvents. This low molecular weight leads to comparatively worse drying and in some cases to unfavourable substrate wetting [3]. Because of this, water-based paint systems are becoming increasingly important.

The water-based polyol types available on the market range from hydroxy-functional alkyd resins and polyesters to high-molecular hydroxy polyacrylates. The hydroxy polyacrylates in particular are

RESULTS AT A GLANCE

→ Water- and solvent-borne 2K PU coatings show comparable properties in terms of high gloss and final hardness as well as excellent scratch and chemical resistance.

→ However, water-borne systems have low curing speeds compared to solvent-borne alternatives. Another limitation is the occurrence of side reactions between polyisocyanates and water. The carbon dioxide formed can produce blistering, and the possible formation of polyureas will reduce gloss.

→ To improve this situation, water-emulsifiable polyester polyols were tested that had an increased molecular weight and/or incorporated tertiary amine functionality.

→ Tests on a white pigmented formulation showed that these modifications gave significant reductions in drying time and initial development of hardness, with no effect on final properties. Gloss and resistance to blistering both remained high.

characterised by excellent drying properties, high saponification and weather resistance as well as excellent colour stability.

In order to ensure an acceptable processability and better handling of high-molecular weight hydroxy polyacrylates, however, it is necessary to use cosolvents. In addition, water-based paints made from hydroxy polyacrylates have a relatively low blistering limit due to the presence of air inclusions [4, 5] and the side reactions of the hardener with water, which result in the formation of carbon dioxide.

If air bubbles and the resulting carbon dioxide remain as inclusions in the paint film beyond the open time, this results in micro-bubbles in the hardened layer of paint, which in turn results in significantly less gloss and in the worst case to a failed coating. This is why in many cases only low film thicknesses can be applied without major problems or bubbles.

Hydroxy-functional alkyd resins meet the high requirements for gloss,

a low tendency to form bubbles and excellent processability. Unfortunately, in many cases saponification and weather resistance are significantly reduced compared to hydroxy polyacrylates. This is why hydroxy polyesters have made a name for themselves as high-quality polyol components.

In addition to the advantages of the hydroxy-functional alkyd resins indicated, this group also has excellent weather and colour stability as well as outstanding hardness development. That is why they are also frequently used as co-binding agents.

LIMITATIONS OF CATALYSIS IN WATER-BORNE SYSTEMS

A major advantage of solvent-based 2K PU coatings is the almost unlimited control of the curing speed due to a targeted use of catalysts, such as DBTL, zinc octoate and amines. These catalysts are simply dosed into the paint formulation and homogenised. The final paint is applied while maintaining the required process time. This adjustment is much more complex for water-based paints, because the addition of the catalyst also automatically triggers the hydrolysis of the isocyanates present (Figure 1). As a result, reactive isocyanate groups are reduced and are no longer available for the cross-linking reaction with the polyol.

An additional problem is the carbon dioxide formed by the hydrolysis, which causes micro-bubbles that can be enclosed inside the coating after application and that irreversibly remain in the film as micro-bubbles after drying. This is why an over cross-linking level is usually employed, i.e. an excess of isocyanate groups.

In addition, the subsequent reaction forming polyurea and its derivatives also poses a risk. If the polyurethane reaction is not selective enough and if this secondary reaction is not sufficiently prevented, there is a significant loss of gloss.

FORMULATING IMPROVED POLYESTER POLYOLS

For the reasons discussed above, different polyester polyols were synthesised and tested with varying property profiles. A standard polyester polyol emulsion served as the starting point here. It is known that the (physical) drying is significantly influenced by the molecular weight of the resin [6]. That is why a molecular weight increase was the first synthesis step. The increase in molecular weight was achieved by a longer condensation time and the addition of aliphatic diisocyanates (modification 1).

In order to allow the reaction between the polyol and hardener to occur as selectively as possible and without side reactions, the covalent incorporation of catalytically active centres was attempted in another test (modification 2).

In the process, a building block was chosen that combines both ter-

Figure 1: Possible secondary reactions of the hardener component in 2K PU coatings: hydrolysis and formation of polyurea.

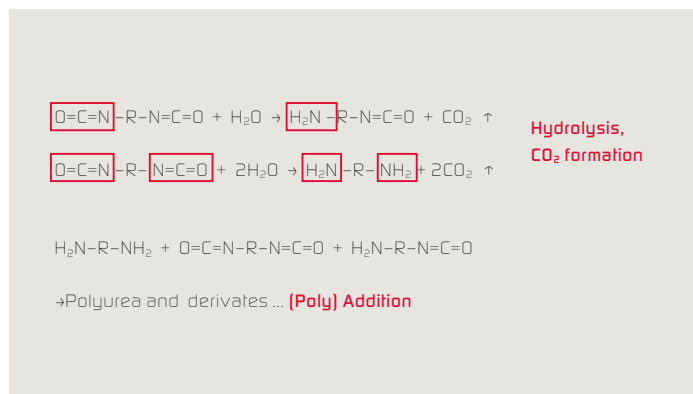
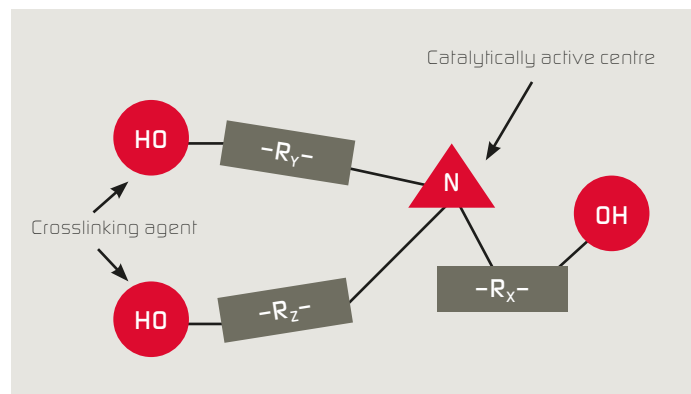


Figure 2: Concept structure of the catalytically active building blocks.



tertiary amine functionality as well as the product class of a polyalcohol. The tertiary amine functionality is a classic polyurethane catalyst, which is intended to locally stimulate the link between the polyol and isocyanate hardener.

The additional hydroxy functionality serves as another branching point here for cross-linking with the hardener. The model structure of the catalytically active cross-linker and the resulting polyester polyols are shown schematically in Figures 2 and 3.

All the test resin polyester polyols can be emulsified in water and do not require any additional stabilisers. Their specifications are summarised in Table 1. The specification ranges are comparable to each other, have a solids content between 38 - 41% and an associated vis-

cosity between 500 - 3,000 mPas. The pH value is nearly neutral and thus is ideal for formulating master batches.

The OH number and thus the density of the potential cross-linking with isocyanate hardeners is 180 mg KOH g⁻¹ for the standard. The new developments based on modification 1 and modification 2 show a somewhat extended range. For modification 2, a slightly increased OH number can be seen compared to the standard, which is a good example of the successful incorporation of the catalytically active cross-linking centres. In order to confirm the strategy of the catalytically active centres and the improved curing speed, a pigmented top coat formulation was developed. Its detailed composition is shown in Table 2.

Figure 3: Structural models of the polyester polyol emulsions tested: standard, modification 1 and modification 2.

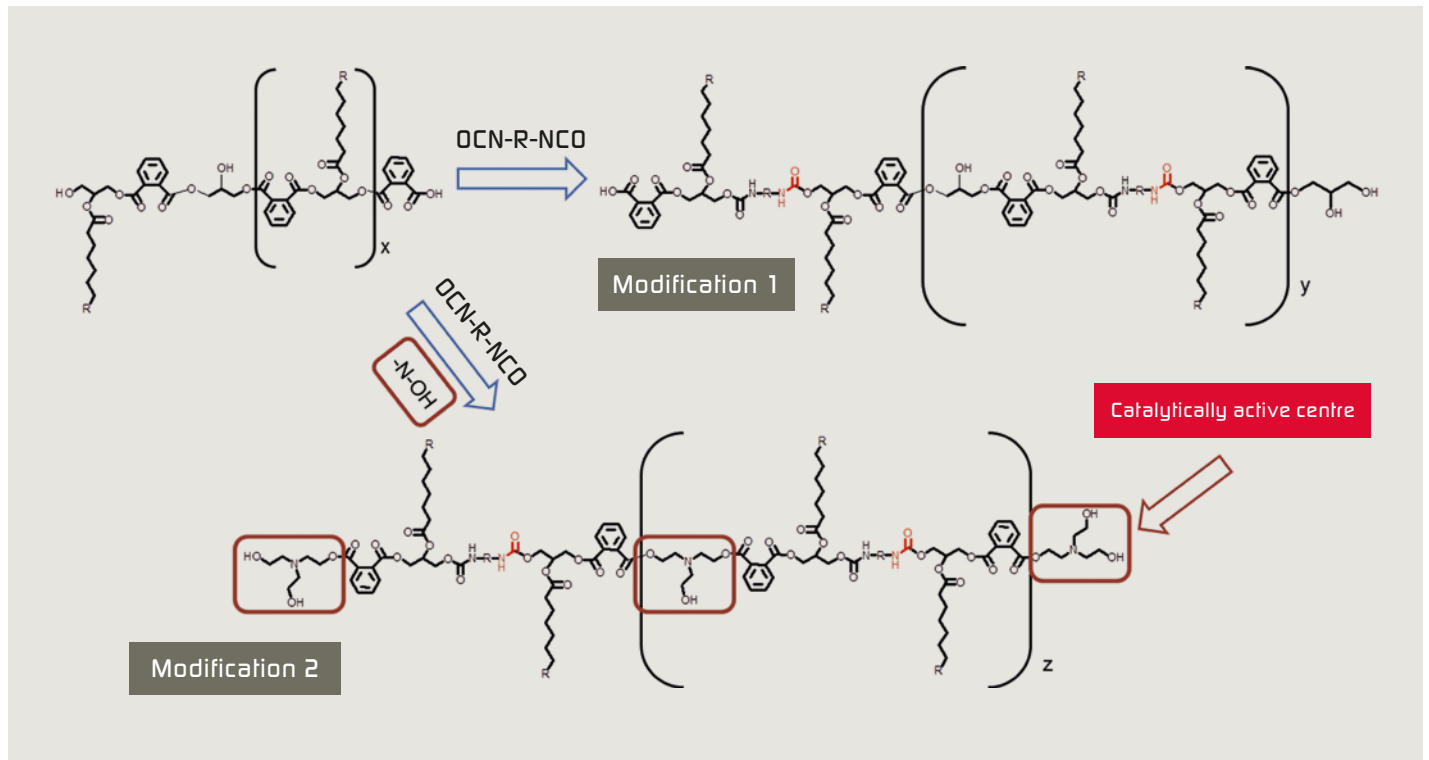


Figure 4: Drying speed comparison for the standard and modified polyols.

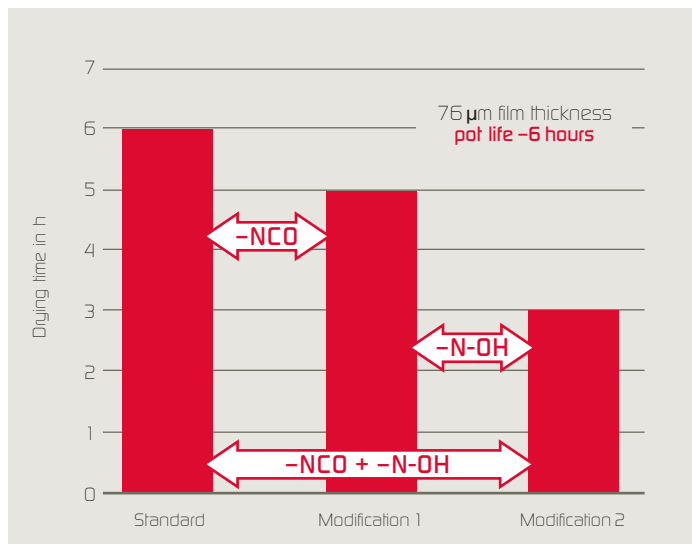
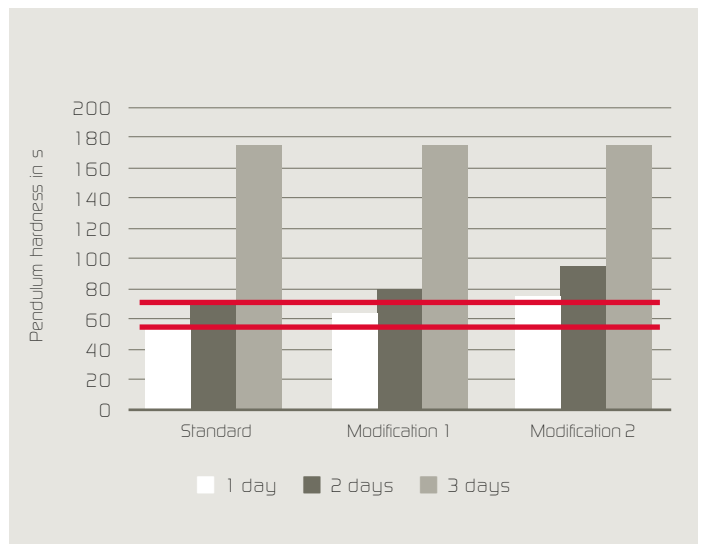


Figure 5: Comparison of König pendulum hardness development over seven days.



FASTER DRYING AND IMPROVED INITIAL HARDNESS

The formulated base coat was mixed with the hardener in the ratio of 4:1, adjusted to a spray viscosity of 30-35 s and prepared for spray application. The pot-life of the final 2K PU coating was determined to be six hours based on loss of gloss, and was thus within the acceptable framework for industrial processes.

To determine the drying time, the different paint systems were used with a film thickness of 76 µm on a glass plate and clamped in a Byk-Gardner drying time recorder. For the objective assessment of the drying time, the time was determined at which the needle of the drying recorder does not leave behind any recognisable trace in the coating.

The drying time for the standard product here was about six hours and was reduced to five hours through the targeted increase of the molecular weight (Figure 4, modification 1). By incorporating the catalytically active centres in the polyol backbone, the drying time was further reduced to three hours with the same starting formulation (Figure 4, modification 2).

This was a halving of the drying time compared to the standard system. This result confirmed the activity of the catalytically active components and their high affinity to the hardener.

FINAL TEST VALUES ARE SIMILAR FOR ALL COATINGS

In order to further examine these results, the hardness development was determined using pendulum damping according to König (6° - 3°, Figure 5). An increase in the molecular weight (modification 1) resulted in a slightly improved hardness development of additional ten seconds after two days (from 70 to 80 seconds). Here too there was a significant improvement of the hardening, especially after two days, for the polyol component with catalytically active centres. The difference from the standard here was about 30 seconds. The catalytically active centres here as well as the adjacent hydroxyl groups acted as three-dimensional branching points and were thus able to form a dense network.

Table 1: Specifications of the polyester emulsions tested.

	Standard	Modification 1	Modification 2
Solids content wt%	38 - 41	38 - 41	38 - 41
Viscosity mPa·s at 25 °C	1000 - 3000	1000 - 3000	500 - 3000
pH value	6.5 - 7.5	6.5 - 7.5	6.5 - 7.5
OH-content wt%	5.5	5.0 - 6.0	5.5 - 6.5
OH number, mg KOH g ⁻¹	Ca. 180	165 - 200	165 - 215
Cross-cut (steel)	GI0	GI0	GI0
Blistering limit µm	Ca. 100 - 150	Ca. 100 - 150	Ca. 100 - 150

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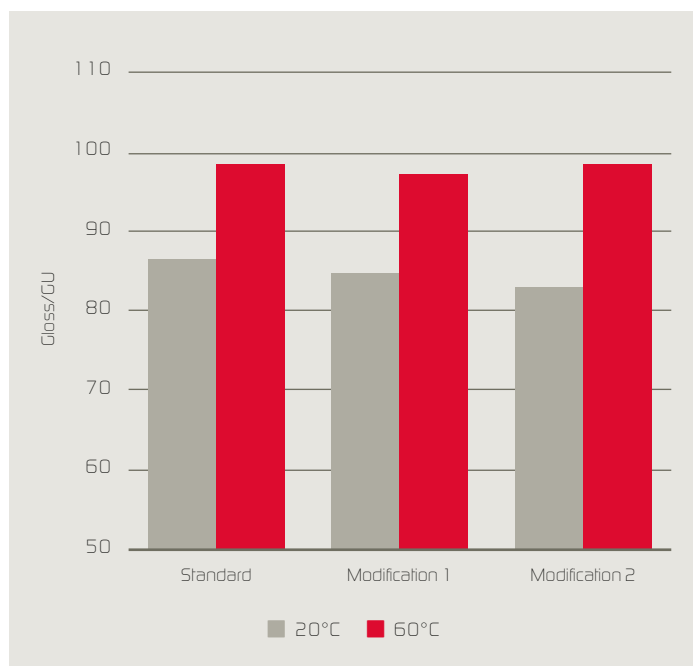
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Table 2: Starting formulation of pigmented 2-pack top coat.

Component	Parts %
Binder	55.68
Pigment paste	31.54
Thickener	0.20
Water	5.35
Wetting/levelling additive	0.65
Levelling additive	0.74
Wetting/levelling additive	0.28
Easy-clean additive	2.78
Flash rust inhibitor	2.78
Total	100.00
Hardener, mixing ratio 4:1	
HDI trimer	80
Butyl glycol acetate	20
Total	100.00

Figure 6: Gloss comparisons at both 60° and 20°.



The final hardnesses after seven days are almost comparable for all systems and clearly demonstrate that the resin modification only stimulates the initial reaction of polyol and hardener due to the incorporation of catalytically active centres.

The deformability and adhesion to steel were determined using the Erichsen deep drawing test. The coating remained intact up to a depth of 8 mm, at which the steel plate itself ripped. Thus a depth > 8 mm was found for all systems, which indicates a sufficiently deformable film and excellent substrate adhesion. This was also verified by cross-hatch testing. All coatings were evaluated as Gt0.

EXCELLENT BLISTERING RESISTANCE AND GLOSS

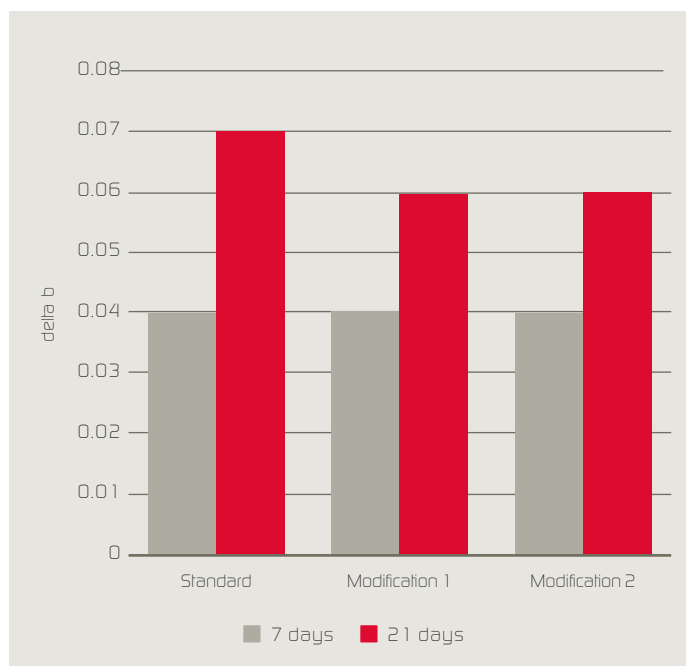
In order to test the blistering limit of the respective paint formulations, the spray viscosity of all systems was set to 30-35 seconds and film thicknesses were applied up to 150 µm by means of spray application. No blistering could be identified up to this film thickness of 150 µm, which indicates excellent process reliability during the application process and subsequent drying. In addition, all coatings have a high gloss character (Figure 6). At 60°, values on average of 97 gloss units (GU) are achieved. At 20°, the values drop to 83-86 gloss units as expected. The colour stability of the resulting coatings under UV treatment was examined by means of QUV-A testing for 21 days. All coatings exhibit very high colour stability with a delta b value below 0.1 (Figure 7).

FASTER DRYING ACHIEVED WITH NO PERFORMANCE LOSSES

The covalent incorporation of catalytically active centres in the polyol component, which can also serve as branching points for the isocyanate cross-linking, is a new way to positively influence the curing speed of water-based 2K PU coatings. The paints produced exhibit accelerated curing as well as an improved hardness development.

The usual advantages, such as high gloss and gloss retention, as well as a low tendency to blistering, remain completely preserved. This development clearly shows that the targeted incorporation of catalytically active cross-linking points is another step in the right direction and this strategy may also be transferable to other classes of resin. ④

Figure 7: Comparison of yellowing resistance after 21 days QUV-A exposure.



“Catalysis of water-borne 2K PU systems is still very limited.”

3 questions to Jan Klesing

The mechanical and technological properties are evident. However, there was no indication of the properties of the coatings when exposed to chemicals. How does this modification to the polyester polyol perform when these stresses are applied? The high OH-number of the polyester polyol emulsion with catalytically active centres allows for improved cross-linking and thus excellent chemical resistance. The resistance to certain test substances was examined, evaluated and compared with suitable competitive products by using the DIN 68861 norm furniture standard. In this test, the chemical resistance of the standard system as well as the new development with catalytically active centres was comparable with conventional systems. The catalytically active centres therefore have no additional effect on the chemical resistance. Accordingly, their primary effect is related only to the improved drying speed.

How does the new polyester polyol behave in the case of forced drying, do the catalytically active centres play a role? The catalytically active centres also have a significant effect after forced drying. Clear-coat formulations in particular show improved hardness development, compared to the unmodified version without catalytically active centres. This result clearly shows that the catalytically active centres react selectively with the hardeners and both the cross-linking and curing behaviour are significantly stimulated. This is a further proof that the concept of the catalytically active centres is effective.

Does this modification mean the possible replacement of conventional catalysts? If so, to what extent? The catalysis of water-based 2K PU coatings is very complex compared to solvent-based systems. Even with subsequent catalysis, water-based types have not yet approached the curing behaviour of highly catalysed solvent-based types. The catalysis of water-based types is still very limited. A fundamental problem here is the side reaction of the hardener with water to form polyurea, its derivatives and carbon dioxide. As a result, excessive amounts of additional catalysts can lead to a significant loss of gloss of the final coating and thus to a loss of important basic properties. The new polyester polyol emulsion is characterised by significantly improved curing behaviour compared to other water-based types. The quantity of additional catalysts used is thus significantly reduced and any loss of gloss is almost completely prevented. It remains to be seen to what extent this new development will affect the amount of additional catalysts used in the future.



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