

Low VOC, high-solids, 2K aliphatic polyurethane systems using novel hydrophobic polyols

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Abstract

Low VOC, high-solids, highly durable, two component (2K) aliphatic polyurethane coatings continue to be of high interest for various markets including General Industrial, Automotive Refinish, Wood Coatings and Plastics. These coatings are applied and cured using ambient or forced cure conditions. Use of nearly 100% solids hydrophobic polyols, offers a pathway towards achieving the low VOC targets for the various markets. We will present information on the characteristics of two such polyols and will present a set of data which includes acid etch, hardness, flexibility and impact resistance.

Introduction

2K polyurethane coatings systems¹ have a wide range of outstanding properties – from excellent film appearance and superior resistance to water, solvents and chemicals, to excellent weathering and good scratch resistance. In addition to the high quality level provided by these properties, the coatings exhibit fast drying and good curing at ambient temperature or under forced drying conditions (RT to 80° C), thus matching the requirements of coatings for general industrial, and automotive refinish applications. The benchmark for high-performance coatings systems has long been considered to be 2K solventborne polyurethane coatings.

However, the growth of these high performance coatings has been limited due to the lack of proven lower VOC alternatives. Governmental regulations continue to set solvent emission levels for paints. Most of these coatings require ambient or low temperature forced curing, thereby limiting the options to achieve compliance with VOC regulations.

The secret of the growing success of these technologies lies in the development of three areas

1. Development of improved, well designed polyol resins;
2. Development of a new generation of low-viscosity crosslinkers; and
3. Development of new application technologies.

The challenge with respect to high solids solventborne low VOC coatings, is to combine reduced solvent content with acceptable application properties, including pot life and drying speed. 2K polyurethane high solids coatings require resins designed for fast drying and excellent appearance despite the reduced molecular weight necessary to achieve low viscosity.

Acrylic Polyol Concepts towards building Low VOC coatings

Challenges in developing Low VOC coatings

- High solids coatings with a dry time/pot life balance, under a variety of conditions are not possible, since these do not first "lacquer dry" prior to complete crosslinking with the polyisocyanate.
- Lower molecular weight high solids coating components, including polyester and acrylic polyols require more reaction time before these obtain sufficient molecular weight to achieve dust free or dry-to-touch conditions.

Application of high solids coatings with conventional equipment, requires sufficiently low coating viscosities that make it necessary to significantly reduce the molecular weight of the binder resin.

However, the approach of reducing molecular weight to achieve a suitable application viscosity has limitations. As molecular weight is reduced, it becomes necessary to increase the ratio of functional monomers in the oligomer to increase crosslinking sites for molecular weight build up. Furthermore, reactive groups tend to be polar and participate in intermolecular interactions such as hydrogen bonding. This tends to increase viscosity, thus offsetting the viscosity decrease desired from molecular weight reduction.

Formulation of high solids systems, requires the proper design of the monomer composition, molecular weight and its distribution, as well as the functionality of a binder resin to achieve a good balance of film properties, durability and formulation viscosity.

This is possible using a process referred to as SGO (Solid Grade Oligomer)². The continuous SGO polymerisation process, as opposed to the more typical batch polymerisation methods, was introduced by S.C Johnson. The SGO process is tailored to produce low molecular weight oligomers and polymers without the need for high initiator levels and foul odour chain transfer agents. In addition, most importantly, the SGO polymerization process yields exceptionally narrow polymer molecular weight distribution. Each oligomer chain produced via SGO has a uniform molecular weight. The narrow molecular weight distribution of SGO produced oligomers is 1.7-2.8 versus the 4-7 distribution, more typical of commercial acrylic polyols. The narrow molecular weight distribution, also referred to as polydispersibility, directly addresses several of the key limitations of typical high solids acrylic and polyester polyols.

The very low molecular weight fractions present in conventional high solids acrylic polyols have a reduced functionality per molecule. These typically dimer/trimer molecules often do not carry an adequate amount of hydroxyl groups for complete matrix crosslinking with polyisocyanates. The uncrosslinked chains tend to soften (or plasticize) the coating, leading to longer drying times as well as poor and/or inconsistent performance. These fractions are also prone to volatilization and sagging, if an oven cured system is used. SGO polymerization virtually eliminates these very low molecular weight fractions, thus helping overcome these typical high solids deficiencies. The absence of very high molecular weight fractions in SGO polyols minimises the paint viscosity at high resin solids and helps improve paint levelling and spray application properties.

Joncryl Polyol blends

In the literature, acrylic polyol copolymer blends³ concepts have been used toward achieving higher solids lower VOC alternatives. While useful, these blends have generally not performed well from an overall performance standpoint, particularly under ambient cured conditions³.

We designed two low Tg hydrophobic polyols Joncryl 960 and Joncryl 963 to blend with high Tg polyols e.g Joncryl 587, Joncryl 804 and Joncryl 906, to achieve a balance of properties and VOC reduction.

In this paper, we will discuss the work carried out in blending Joncryl 960 or Joncryl 963 with Joncryl 906.

Polyols

Table 1

Polyol	Tg (°C)	% solids	solvents	Equivalent Weight
Joncryl 906	16	72	MAK	600

Joncryl 906 (Table 1) was chosen for this study because of its ability to produce outstanding gloss retention, dry time and pot life balance for high performance maintenance and transportation finishes.

Joncryl 960 and Joncryl 963 (Table 2) are two hydrophobic polyols supplied at more than 98% solids. Both resins are hydroxyl functional acrylics for flexibilizing the high performance automotive and industrial markets. The molecular structure of both polyols offers an advantage

for VOC reduction, improved weathering and acid-etch resistance. In addition, Joncryl 960 also offers increased flexibility.

Table 2

Polyol	Equivalent weight	Solids (wt %)	Viscosity(cP)
Joncryl 960	675	98 +	21200
Joncryl 963	432	98 +	11250

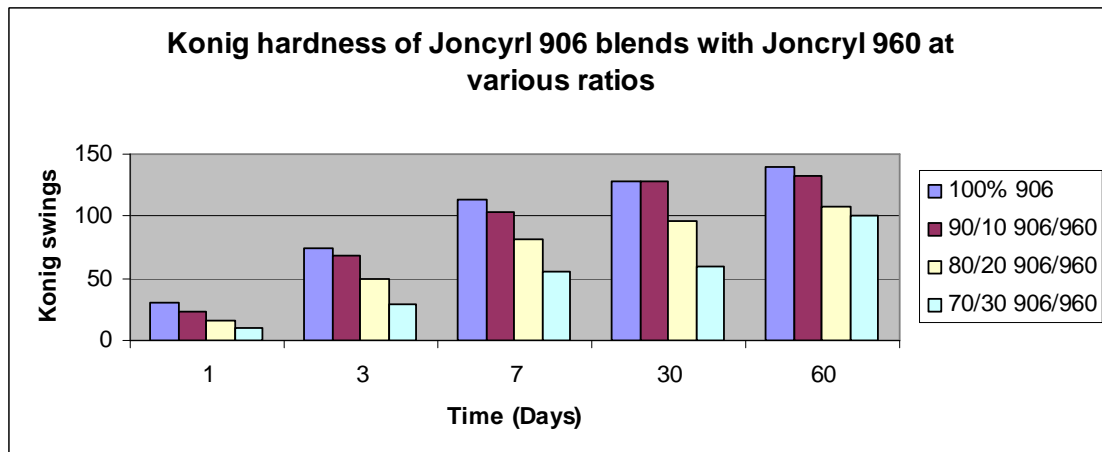
Joncryl 906 was blended with Joncryl 960 at three ratios of 90/10, 80/20 and 70/30 based on equivalent weight. The blends were made into clearcoat formulations using Basonat® HI 100(hexamethylene diisocyanate). Panels prepared by applying acrylic urethane clear finishes on steel panels at a thickness of 1.5 mil using a #40 wirewound bar, were allowed to reach full cure by aging at ambient conditions for 30 days. All formulations used Basonat® HI 100 at a 1.05:1 isocyanate index. The only additives used in the formulations were 1% DBTDL(solution in methyl amyl ketone) & BYK 333 polyacrylate leveling agent. Each of the compositions were evaluated for pot life and film properties e.g hardness using Konig swings. Flexibility was measured using direct impact, reverse impact and conical mandrel bend.

Table 3

Polyol Blend	J 906	J 960	VOC
1	100%	0%	3.7
2	90%	10%	3.5
3	80%	20%	3.4
4	70%	30%	3.3

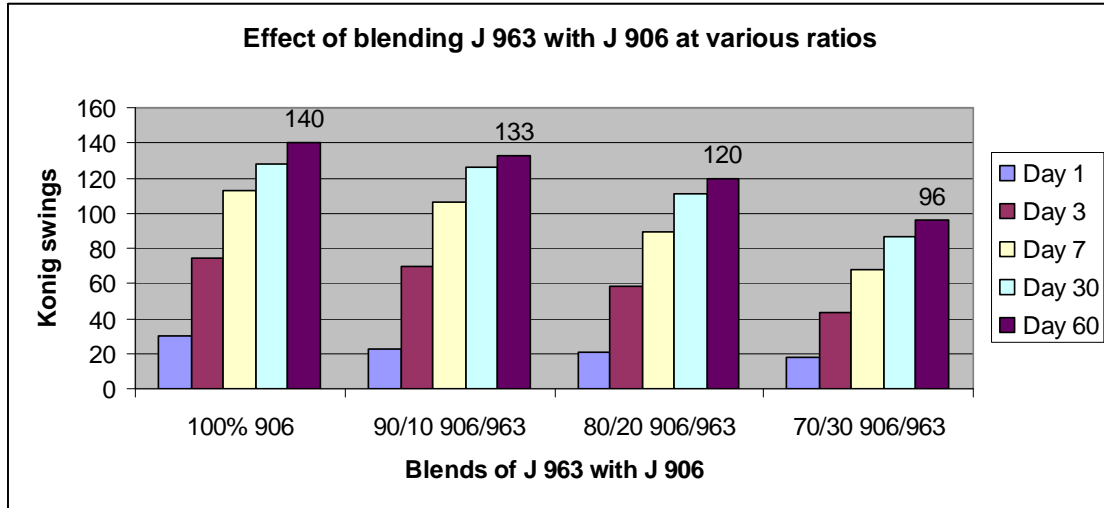
As shown in Table 3, in blends of Joncryl 906 with 960, Joncryl 960 acts as a reactive diluent effectively lowering the VOC of the activated acrylic urethane clear coating. A 30% modification lowers VOC by 0.4 pounds per gallon based on the amount of methyl amyl ketone needed to lower viscosity to 200 cps using a Brookfield viscometer.

Graph 1



Graph 1 compares the Konig hardness using blends of Joncryl 906 with Joncryl 960 at 10% increments based on equivalent weight. Note minimal loss of film hardness is measured based on the number of swings using this hardness method. Even at 30% modification, films have excellent hardness (100 swings) after 60 days.

Graph 2



Graph 2 compares the Konig hardness using blends of Joncryl 906 with Joncryl 963 at 10% increments based on equivalent weight. Note minimal loss of film hardness is measured based on the number of swings using this hardness method. Even at 30% modification, films have excellent hardness (96 swings).

Table 4

Polyol Blend	J 906	J 963	VOC
1	100%	0%	3.7
2	90%	10%	3.6
3	80%	20%	3.5
4	70%	30%	3.4

As observed in Joncryl 906 combined with 960, in Table 4, Joncryl 963 is shown to act as a reactive diluent effectively lowering the VOC of the activated acrylic urethane clear coating. A 30% modification lowers VOC by 0.3 pounds per gallon based on the amount of methyl amyl ketone needed to lower viscosity to 200 cps using a Brookfield RV viscometer.

Table 5
IMPACT Test

Direct Impact							
	100% 906	960			963		
Time (days)	100% 906	90/10	80/20	70/30	90/10	80/20	70/30
7 day	20	20	120	>160	40	40	80
30 day	<20	120	>160	>160	60	60	60
Indirect Impact							
	100% 906	960			963		
Time (days)	100% 906	90/10	80/20	70/30	90/10	80/20	70/30
7 day	<20	<20	<20	>160	<20	20	<20
30 day	<20	60	20	>160	<20	40	20

Blending Joncryl 960 & 963 effectively increase flexibility of the cured films as indicated in direct and indirect impact measurements as shown in Table 5. A 30% modification of 906 with 960 increases both forward and reverse impact in excess of 160 in-lbs. Joncryl 963 has a less dramatic effect at 30% modification, but still increases impact resistance greater than 300%.

Table 6

Pencil Hardness							
	100% 906	960			963		
Time (days)	100% 906	90/10	80/20	70/30	90/10	80/20	70/30
3 day	H	H	H	H	H	H	H
7 day	H	H	H	H	H	H	H
30 day	2H	2H	2H	H	2H	2H	2H

Little effect on pencil hardness is observed up to a 30% modification (Table 6). These results are in agreement with minimal check in surface hardness as measured using the pendulum damping method, Konig.

Table 7

	Distance to end of crack/%Elongation corrected for film thickness						
	Conical Mandrel	960			963		
Time (days)	100% 906	90/10	80/20	70/30	90/10	80/20	70/30
7 day	NC/>32	NC/>32	NC/>32	NC/>32	NC/>32	NC/>32	NC/>32
30 day	NC/>32	NC/>32	NC/>32	NC/>32	NC/>32	NC/>32	NC/>32

Conical mandrel measurements are inconclusive (Table 7). No cracking was observed even with no modification with Joncryl 960 or 963. All films had > 32% elongation.

Table 8

	MEK Rub						
	100% 906	960			963		
Time (days)	100% 906	90/10	80/20	70/30	90/10	80/20	70/30
1 day	5	3	5	5	3	3	3
3 day	20	18	20	20	10	10	15
7 day	40	50	48	40	60	40	40
30 day	90	80	80	70	85	70	60

Some loss of methyl ethyl ketone resistance is noted as indicated by a slight decrease MEK double rubs (Table 8). This is expected based on the incorporation of more linear acrylic oligimers which slightly decreases cross-link density.

	Gardner Dry-Time						
	100% 906	960			963		
Time (days)	100% 906	90/10	80/20	70/30	90/10	80/20	70/30
Set-to-Touch	1	0.5	0.5	1.5	1	0.5	0.5
Tack-Free	11	10.5	12	11.5	16	4	16
Dry-Through	18	18	18	17	20	20	18
Dry-Hard	23.5	22.5	22	22.5	23	23	23.5

Most flexibilizers have a significant affect on dry times. Very little affect on dry times was noted on Gardner Dry-Time recorders using blends of Joncryl 906 with 960 & 963.

Acid etch resistance

Acid rain resistance is an important performance feature for automotive finishes. Presently, the most accepted method of testing acid rain resistance involves the exposure of coated plastic panels on Blount Island near Jacksonville Florida. A method described by BYK Instruments which details the use of dilute aqueous acids & a gradient oven to quantify the acid rain resistance of finishes was used to evaluate the polyols in 2 K acrylic urethanes.

Panels prepared by casting acrylic urethane clear finishes on untreated cold rolled steel panels using a 200 µm draw down bar were allowed to reach full cure by aging at ambient conditions for 30 days. All formulations used Basonat® HI 100 at a 1.05:1 isocyanate index. The only additives used in the formulations were 0.005% DBTDL & 0.5% BYK 361N polyacrylate leveling agent.

A gradient oven set for a 30 min. time cycle using a temperature range of 35 - 75°C as a continuous gradient was used. The oven has 45 individual temperature zones. Panels were labeled with paper strips numbered 1 to 45 corresponding to the 45 individual temperature zones. Directly opposite each of the 45 zones, 2 drops of 10% sulfuric acid solution was placed using a disposable pipette and the panel was moved gently onto the preheated gradient surface. At the end of 30 minutes, any residual sulfuric acid solution was rinsed off with tap water. The effect of the acid solution was recorded. The minimum spot temperature (MST, Table 10 Graph 3) was recorded. To make the faintest rings visible, exhale, as if cleaning glasses, over the rings to determine where "grade 1" damage begins. Assign a grade value to each of the 45 temperature zones and add all values. This is the total acid score (TAS, Graph 3). Each zone is graded based on the following parameters.

Grading System

Grade 0 - no affect, Grade 1 - barely visible, Grade 2 - complete circle visible, but not filled in, Grade 3 - circle fully visible & filled in, Grade 4 - blistering evident

Grade 5 - removal of film to bare metal .

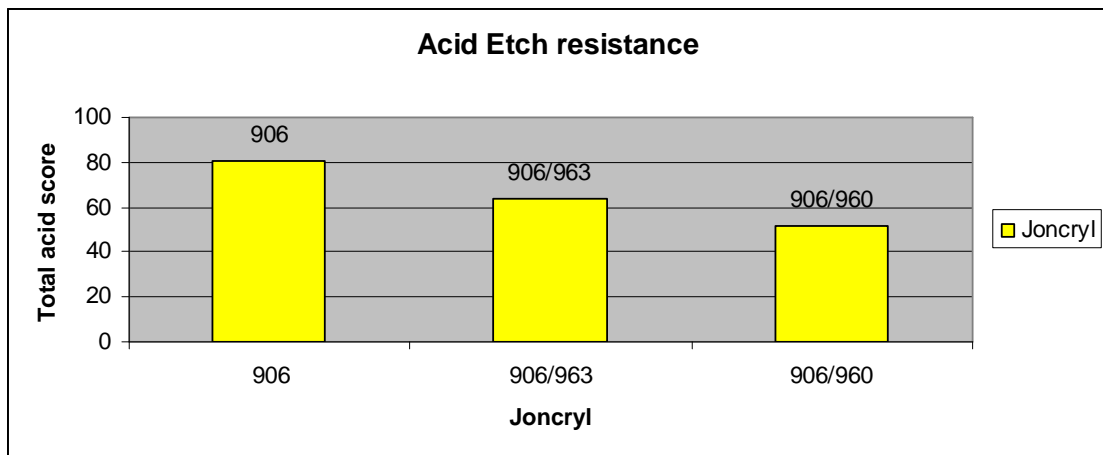
A score of 225 would indicate complete failure starting in temperature zone 1. Results are given in Table 10.

Table 10

Polyol	Min. Spot Temperature		Total Acid Score	
	Initial	After 24 Hrs.	Initial	After 24 Hrs.
906	55	55	76	81
70:30 906/960	59	64	57	52
70:30 906/963	58	61	67	64

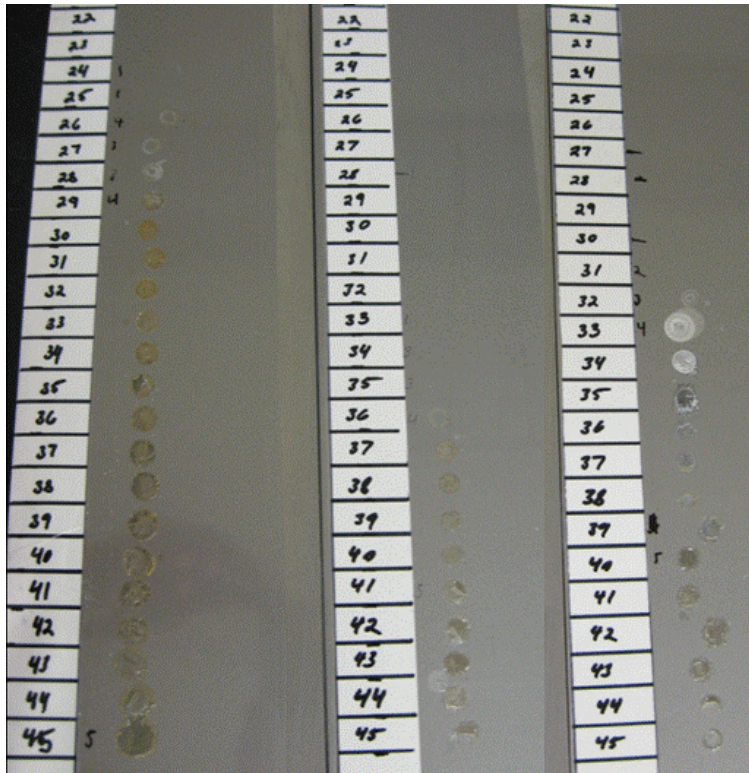
The addition of Joncryl 960 or 963 dramatically increases the film's resistance to dilute sulfuric acid as indicated in the above table 9 Graph 3 and Figure 1. Results are given after initial removal from the gradient oven as well as after 24 hour recovery.

Graph 3



TAS (Total Acid Score) = the summation of all grade scores at each of the 45 temperature zones in the gradient oven.

Figure 1



Joncryl 906

Joncryl 906/960 Joncryl 906/963

Overall, this test method is a good tool for determining acid etch resistance & is consistent with data described from some of our customers.

Also noted is that J960 greatly increases the acid etch resistance of J906 in this study. This method may be useful for chemical resistance testing using other chemical solutions.

Acrylic Replacement for Caprolactones

Joncryl 960 and 963 were developed as modifiers to give acrylic urethanes finishes caprolactone-like properties. Caprolactone-based polyols are known to have excellent flexibility. Caprolactone polyols have drawbacks as these are expensive and are incompatible with some resins. In Table 11, the comparison of the properties of acrylic polyols to caprolactone 320 is shown.

Characteristics	Joncryl 960	CAPA 3201
Equivalent weight	675	668
Resin viscosity	14,500 cP pourable liquid	soft wax
Joncryl 901 clearcoat with 10% modification with Joncryl 960		
Clearcoat viscosity at 3.2 lbsa/gal VOC	168 cP	164 cP
Hardness development		
24 hours	9	11
7 days	86	72
Gardner hard dry time (hours)	8	6.5
Impact resistance(in-lb)		
direct	150	160
reverse	160	160

Conclusions

Low VOC, high-solids, highly durable, 2K aliphatic polyurethane coatings have been developed using blends containing almost 100% acrylic polyols-Joncryl 960 and Joncryl 963. Use of Joncryl 960 or 963, offers a pathway towards achieving the low VOC targets for the various markets. Blending hydroxyl functional acrylic resins and soft, low Tg, more linear structured polyols like Joncryls 960 and 963 allows the formulator to "dial-in" the desired properties and produces coatings suitable for a wide range of applications and coating technologies. We have developed starting formulations for industrial maintenance, and automotive refinish. . Further work, using an Instron, is planned to further quantify the increase in flexibility when blending Joncryl 960 & 963 with various other Joncryl polyols. These new acrylic polyols will help formulators meet the ever-increasing performance, compliance, and economy requirements for coatings.

Contributors

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