Polyurethane Rigid Foams From Agrol® Polyols

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ABSTRACT

Characteristics of Agrol® products from BioBased Technologies®, formulations, formulation strategies and properties of rigid foam systems, based on these soybean oil polyols are presented. Water blown (0.5, 3.0, 6.0 pcf) and HFC 245fa blown (2 pcf) spray systems and a water blown open pour (6 pcf) system are easily prepared with 7 to 24% biocarbon contents.

INTRODUCTION

Agrol® polyols are hydroxylated triglycerides derived from refined soybean oil using a patented oxidation process. They are used in many different polyurethane applications where their properties can be described as ranging from semi-flexible to semi-rigid. Five polyols, containing secondary hydroxyls, form a spectrum of products with hydroxyl values ranging from 70 to 190 mg KOH/g and biocarbon contents, as measured by ASTM D6866 of 99%. A life cycle analysis of polyols by Omni Tech International [1] has concluded that Agrol® polyols have a beneficial impact of 5.6 pounds of CO_2 to the atmosphere for every pound that replaces a pound of petroleum polyether polyol. Two additional products are produced by further modification of the Agrol® structure to give primary hydroxyl groups. Agrol Diamond® is a 3 functional polyol, containing approximately 70% primary OH, and at a 350 hydroxyl number, represents BioBased Technologies'® lowest equivalent weight product. As a result of the petroleum modification, the biocarbon content at 86%, as measured by ASTM D6866, is lower than those of the main product line. Agrol® 3-165 is a soy-based polyol designed to give similar functionality, equivalent weight, hardness and reactivity to castor oil. The biocarbon content for this product is 96%.

Table 1: Properties of Agrol® Polyols

Property	Units	Agrol® 2.0	Agrol® 3.6	Agrol® 4.3	Agrol® 5.6	Agrol® 7.0	Agrol Diamond®	Agrol® 3-165
OH Value	mg KOH/g	65 - 75	107 - 117	125 - 137	151 - 170	175 - 195	335 - 365	160 - 170
Acid Value	mg KOH/g	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0
Viscosity, 25ºC	cP	233	720	1320	4770	21,500	3500	1500
Water Content	% w/w	≤0.1	≤0.1	≤0.1	≤0.1	≤0.1	≤0.2	≤0.1

POLYOL CHARACTERISTICS

One concern when formulating ester containing polyols with water and basic amine catalysts is the hydrolytic stability of the ester groups. Hydrolysis causes increasing acidity with time, which in turn means slower reactivity with isocyanates due to catalyst deactivation. However, the rate of hydrolysis of the ester bonds in Agrol® polyols in blends containing a few parts of water should be retarded due to the hydrophobic nature of the molecule. The following plot of acid number versus time in a compatibilized blend containing Agrol® 5.6, 5 parts by weight of water and 0.5 parts by weight of triethylene diamine (TEDA) catalyst, shows that although there has been an increase in acidity, the acid number remains well within the specification of ≤1.0 mg KOH/g after 90 days.

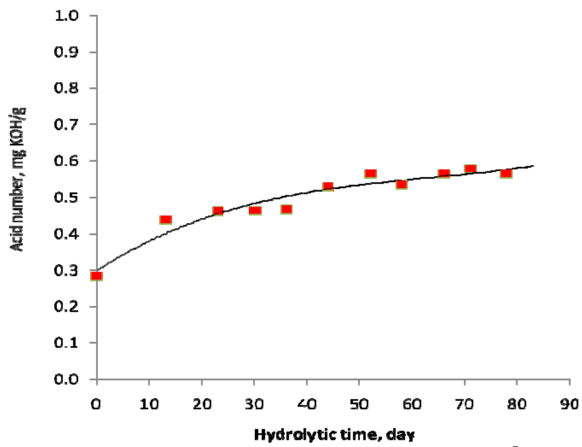

Figure 1: Hydrolytic Stability of Agrol® 5.6

Despite the high hydrocarbon content of Agrol®, the molecular structures contain sufficient polar groups (hydroxyls and esters) to make them very compatible with many of the workhorse petroleum polyether polyols used in typical urethane formulations. Polyesters, which have limited solubility in polyethers, also have limited solubility in Agrol® polyols. This is not to say that B-side blends containing esters and Agrol® products cannot be made compatible. Mannich polyols, in many instances, go a long way to enhance compatibility. For example, HFC 245fa-containing blends which also contain nonylphenol-based Mannichs, are able to incorporate aromatic ester polyols and Agrol Diamond® in a 2:1 weight ratio. These blends are clear and can be formulated to produce 2 pcf spray insulation rigid foams with excellent processing and R-values. Table 2 shows the compatibility of some commercial petroleum polyols with Agrol® products.

Table 2: Compatibility of Agrol® Products with Petroleum Polyols

Petroleum Polyol	**Agrol ® 2.0**	**Agrol ® 3.6**	**Agrol ® 4.3**	**Agrol ® 5.6**	**Agrol ® 7.0**	**Agrol Diamond®**
Mannich Polyol (425 OH No.)			**X**	**X**	**X**	**X**
Terate® 4020						
Glycerin Polyol (240 OH No.)	**X**	**X**	**X**	**X**	**X**	**X**
Glycerin Polyol (470 OH No.)			**X**	**X**	**X**	**X**
Slabstock Polyol (56 OH No.)	**X**	**X**	**X**	**X**	**X**	**X**
Sucrose/Glycerin (360 OH No.)			**X**	**X**	**X**	**X**
Glycerin Polyol (650 OH No.)					**XX**	**XXX**
PPG 1000 (112 OH No.)	**X**	**X**	**X**	**X**	**X**	**X**
Glycerin PO/EO Polyol (28 OH No.)	**X**	**X**	**X**	**X**	**X**	**X**
Ethylene Diamine Polyol (449 OH No.)	**X**	**X**	**X**	**X**	**X**	**X**

X denotes clear blend at both 25/75 and 50/50 Agrol®-to-Petroleum ratio
XX denotes clear blend at 50/50 ratio but phase separation at 25/75 ratio
XXX denotes clear blend at 50/50 ratio and cloudy but non-separating blend at 25/75

To illustrate the range of hardness and tensile strength properties for five Agrol® products, solid polyurethane plaques were prepared from a polymeric MDI-based formulation and B-sides consisting of 26 parts of a sucrose/glycerin polyether polyol and 74 parts of each selected Agrol® product. The range of tensile strengths (300 to 4800 psi) and shore D hardness

(32 to 80) are shown in Table 3. Polyurethane coupons for the Agrol® 4.3 and Agrol® 5.6 formulations were submerged in 40ºC water for 13 weeks with tensile strengths being measured periodically. No significant decrease in these values was observed, implying no hydrolytic decomposition of the polymers during this period.

Table 3: Formulation and Properties of Solid Polyurethanes					
Formulation	**Agrol® 2.0**	**Agrol® 3.6**	**Agrol® 4.3**	**Agrol® 3-165**	**Agrol® 5.6**
Sucrose/Glycerin Polyol	26	26	26	26	26
Agrol® Product	74	74	74	74	74
Total Polyol	100	100	100	100	100
Polymeric MDI (100 Index)	34.5	42.2	44.8	51.1	50.2
Physical Properties					
Initial Tensile Strength (psi)	297	1696	2679	2938	4814
Tensile Strength (psi) after 13 Weeks Aged - 40ºC Water			2673		5006
Initial Elongation (%)	16	16.5	10.9	9.9	9.1
Hardness (Shore D)	32	55	63	66	80

In a second set of experiments, compressive strengths were measured on 1.65 pcf pour-in-place flame retarded rigid foams formulated with each of six Agrol® products. The systems were processed at a 1:1 volume ratio of isocyanate to polyol blend. The compressive strengths ranged from a low of about 9.8 psi for Agrol® 2.0 to a high value of 16 psi for Agrol Diamond®. The B-side blend comprised 30 parts of a sucrose/glycerin polyol, 35 parts of Agrol®, 17 parts of TCPP flame retardant, 4 parts of water with the remainder being amine catalyst and organo and silicone surfactants. In another set of experiments, glycerin/propylene oxide polyethers of differing OH numbers replaced the Agrol® products to produce foams of equivalent compressive strengths. Table 4 compares the Agrol® products to their glycerin polyol counterparts. Thus in this particular formulation, we see that Agrol® 4.3 produces similar compressive strength as the 168 OH Number glycerin polyol. In many cases blends of two commercial glycerin polyols were necessary in order to achieve the equivalent compressive strength. Thus Agrol Diamond® results in similar compressive strength as a 50/50 mix of 470 and 650 OH number glycerin polyols. From the data, one can conclude that the molecular structure for Agrol® polyols are more rigid than the polyethers since in most cases the hydroxyl number of the Agrol polyol which results in equivalent foam strength is significantly lower than the polyether polyol. This is certainly understandable for the case of Agrol® 5.6 and Agrol® 7.0 which have crosslink densities higher than their glycerin counterparts, but the other Agrol® products (Agrol® 4.3, Agrol® 2.0, Agrol Diamond®) have crosslink densities equal to or less than the glycerin analogues. One explanation is the stiffer hydrocarbon chains in soy polyols compared with the more freely rotating ether linkages of the glycerin compounds. In addition, the hydroxyls in the polyethers are telechelic (at the chain ends) rather than randomly placed on the backbones like soy polyols. This provides more flexibility for the polyethers by placing more of the soft phase between the urethane bonds.

Table 4: Glycerin/PO Polyether Polyols (35 pph) Replacing Agrol® Polyols (35 pph) in 1.65 pcf PIP Formulation (1:1 by volume A:B) to Produce Equivalent Compressive Strength Foams					
Agrol® Products	**OH No.**	**Iso Index**	**Glycerin Product(s)**	**OH No.**	**Iso Index**
Agrol® 2.0	70	119	Gly/PO 56, Gly/PO 112 (50/50)	84	118
Agrol® 3.6	112	115	Gly/PO 56,Gly/PO 112 (20/80)	101	116
Agrol® 4.3	131	113	Gly/PO 168	168	110
Agrol® 5.6	160	110	Gly/PO 168, Gly/PO 240 (50/50)	204	106
Agrol® 7.0	185	108	Gly/PO 240	240	103
Agrol Diamond®	350	99	Gly/PO 470, Gly/PO 650 (50/50)	560	83

AGROL® PRODUCTS IN RIGID FOAM

Agrol® 3.6 in Open Pour Rigid Foam (Fake Rock)

A formulation is shown using Agrol® 3.6 in a low density, semi-structural foam. This is an open pour system that can be molded at a 6.0 pcf density to form complex shapes such as those used for furniture or faux (fake) rock applications. Fake rocks are used for landscaping or for hiding utility or telephone boxes, manhole covers, backflow preventers, etc.

Table 5: Agrol® 3.6 in Open-Pour Rigid Foam	
Polyol	**Parts by weight**
Agrol® 3.6	40
Mannich (425 OH No.)	10
Sucrose/Glycerin (360 OH N0.)	42.7
Glycerin	5
Silicone Surfactant	0.9
TEDA (gel catalyst)	0.2
DMEA (blow catalyst)	0.08
Water	1.37
Isocyanate	
Polymeric MDI (31.7% NCO)	110

This system is designed for a 1:1 by volume mix ratio and is formulated to have a long cream time allowing large complex molds to be adequately filled. Agrol® 3.6 is the soy polyol of choice to keep the blend viscosity low. The biocarbon content on the finished foam is 24% by calculation. Flame retarded foams can also be formulated. In this case Agrol® 5.6, a higher functional and lower equivalent weight polyol than Agrol® 3.6, is recommended to maintain foam strength in the presence of the plasticizing TCPP. The reactivity and properties for the above formulation are listed in Table 6.

Table 6: Processing and Properties of Agrol® 3.6 Containing Open-Pour Rigid Foam	
Hand-mix Processing	
Cream Time	50 sec
Gel Time	162 sec
Tack Free Time	252 sec
Mold Temp.	ambient
Demold Time	13 min.
Free Rise Density	4.3 pcf
Properties	
Blend Viscosity (25ºC)	2230 cP
% Biocarbon (foam)	24.1
Compressive Strength (Handmix Foam)	48 psi

Agrol® 4.3 in 0.5 pcf Spray Insulation Foam

Half pound spray rigid polyurethane foams are accomplished by using a high loading of water (15 to 25 parts) on the B-side. Blends of commercial rigid or flexible polyether polyols with Agrol® 4.3 together with standard phosphorus and halogen flame retardants and blow / gel catalysts can produce excellent processing half pound systems using a 1:1 volume ratio of polymeric MDI to B-side component. If a rigid, high crosslink density polyether is not used, a large quantity (> 2 parts) of stabilizing silicone surfactants should be used to avoid foam collapse. Although single phase polyol blends can be accomplished with the aid of organo surfactants, B-side emulsions are recommended instead for longer shelf life stability. Blends that maintain reactivity for six months are achievable despite the high water levels and amine catalysts which have the potential for increasing acid values. Viscosities of 1000 cP or less are also possible allowing for easy processing at standard operating temperatures (115 to 130ºF). The properties of a proprietary system are shown in Table 7.

Table 7: Agrol® 4.3 in 0.5 pcf Spray Foam	
R Value (1in.)	3.7 hr.- ft^2-ºF / BTU
R Value (3.5 in.)	13 hr.-ft^2-ºF / BTU
Compressive Strength	1.24 psi
ASTM E84	Class I
B- Side Viscosity (25ºC)	950 cPs
% Biocarbon in finished foam at 17 parts Agrol® 4.3 on B-Side	11%

Agrol® 5.6 in 3 pcf / 6 pcf Water-Blown Spray Foam Sealants

Water blown, closed cell, spray sealants at 3 pcf and 6 pcf densities are easily formulated with Agrol® 5.6. These products are ideal as vapor retarders, air barriers and insulation in agricultural and industrial applications such as poultry houses, barns, tanks, silos, industrial duct work, etc. About 30 parts of Agrol® 5.6 can be blended with other rigid polyols like Mannich, glycerin or sucrose-based polyols to give biocarbon contents of 15% on the finished foam. For 3 pcf and 6 pcf foams, 2 phr and 0.5 phr of water, respectively are used. If flame retardancy is required, standard phosphorus and halogen additives can be employed. Properties for proprietary 3 pcf and 6 pcf systems sprayed at a 1:1 by volume ratio of polymeric MDI to polyol B-side blend are shown in Table 8.

Table 8: Reactivity and Properties of 3 and 6 pcf Water Blown Spray Foams		
Hand Mix Reactivity	3 pcf foam	6 pcf foam
Gel Time	12 sec.	16 sec.
Tack Free Time	21 sec.	25 sec.
Properties		
Water Vapor Permeability at 1.5 in.	<1 perm	
Water Vapor Permeability at 0.5 in.		< 1 perm
Closed Cell Content	>90%	>90%
Compressive Strength (Hand Mix)	30 psi	78 psi
Biocarbon Content (finished foam)	15%	15%
Dimensional Stability (180º F, ambient humidity)	<1%	<1%
Dimensional Stability (73º F, 50% relative humidity)	<1%	<1%
Flame Property (ASTM E84)	Class I	Not Rated
Initial R-Value	R = 5 at 1 in	R = 1.25 at 0.25 in.

Agrol Diamond® in HFC 245fa Blown Spray Rigid Foam

Agrol Diamond® is the soy polyol recommended for boosting biocarbon levels in HFC 245fa foams because of its solubility in the blowing agent. To achieve a 2 pcf density, 10 parts of HFC 245fa are used in addition to the required amount of water to achieve the target density, generally less than 2 parts by weight. Although soy polyols are not generally miscible with petroleum based polyesters, up to 35 parts of aromatic polyester can be used with no compatibility problems. Mannich and sugar based polyols can also be successfully blended to aid in processing and boosting biocarbon levels. Agrol Diamond® at 16 parts by weight on the B-side blend will result in a biocarbon content of 7% for the finished foam if no other bio materials, like sucrose polyols or glycerin, are used. Combinations of tin and amine catalysts give excellent processing. Finally, phosphorus and halogen flame retardants can be used to meet flame retarding requirements. Initial R values of 6.5 hr-ft^2-ºF / BTU have been measured at 1 inch.

Summary

Formulations and formulation strategies for incorporation of Agrol® polyols into a variety of polyurethane rigid foam systems have been presented. The compatibility of these soy-based polyols with polyethers makes partial substitutions of Agrol® products for the petroleum-based polyols an easy process. The broad range of equivalent weights and functionalities available in the Agrol® product line, also gives the formulator more choices in designing a system that meets the requirements of his application. Water-blown or partially water-blown systems formulated with Agrol® have been shown to remain stable in regard to reactivity in excess of six months. For 0.5 pcf foams, where water is present in unusually high amounts, it is recommended to formulate multi-phase B-side blends to ensure long shelf-life stability. For HFC 245fablown systems, where blend mixing is not possible and single phase B-sides are required, Agrol Diamond® is the product of choice because of its compatibility with this blowing agent. Finally, Agrol® polyols are high in both carbon and biocarbon contents (99% biocarbon for Agrols® 2.0 through 7.0 and 86% biocarbon for Agrol Diamond®) making substitutions into petroleum polyol blends very efficient in increasing the bio-based content of rigid foams. This has significance for lowering the Global Warming Potential of these products. Omni Tech International [1] has concluded that 5.6 pounds of carbon dioxide are removed or prevented from entering the atmosphere for every pound of Agrol® that replaces a pound of petroleum based polyether polyol.

References

1. Omni Tech International. February 2010. "Life Cycle Impact of Soybean Production and Soy Industrial Products," Report Prepared for The United Soybean Board.

Biographies

Neil Nodelman has been at BioBased Technologies® since September, 2008 and holds the position of Technical Director. He received his Bachelor's degree in chemistry from Rutgers University in New Brunswick, New Jersey and his Doctorate in Organic Chemistry from the University of Illinois in Urbana, Illinois. Upon completion of a Post Doctoral fellowship in the Department of Chemical Engineering at the University of Illinois, Neil joined the Bayer Corporation (formerly Mobay Chemical Corporation) as a Senior Chemist in Process Research, where his chief responsibility was development of new polyether and polyester polyols for polyurethane applications. After five years he was transferred from New Martinsville, West Virginia to Pittsburgh, Pennsylvania where he worked on formulating polyurethane systems for a wide variety of applications in the Polyurethane Research Department and later in Business Development. Neil holds 35 U.S. patents in the field of polyurethanes and retired as a Principal Scientist after 33 years from BayerMaterialScience.

Luke Hall has been at BioBased Technologies® since June, 2008 and holds the position of Formulation Chemist. He received his Bachelor's degree in 2007 in Biological Engineering from the University of Arkansas in Fayetteville. In 2011, Luke received his Master's degree in Environmental Engineering, also from the University of Arkansas. Luke has worked on a number of sustainability related projects for BioBased Technologies and more recently has been developing systems for spray foam insulation.

Jianghong Qian has been a Senior Chemist at BioBased Technologies® since 2007 and is technically supporting various Agrol® application projects, such as flexible foam. Jianghong obtained a Masters degree in Analytical Chemistry from the University of Pittsburgh in Pittsburgh, Pennsylvania in 2000. She has previously worked as an analytical chemist for the Nutrition Center at the Arkansas Children Hospital in Little Rock, Arkansas. During 2002 – 2004, Jianghong worked as a bioanalytical chemist at the Virginia Bioinformatics Institute in Blacksburg, Virginia.

Will Parker was an Applications Technician at BioBased Technologies® from July, 2007 through June, 2011. He is currently employed at Central Spray Systems in Springdale, Arkansas.

Nikki Shackelford has been a Formulation Chemist at BioBased Technologies® since April, 2008. She received her Bachelor's degree in Chemistry in 2010 from the University of Arkansas in Fayetteville. Nikki also holds a Bachelor's degree in Criminal Justice and Sociology from the University of Arkansas. She has worked extensively with the Agrol® product line, developing spray foam insulation and other rigid foam systems with high bio-content. Nikki is also assisting customers to formulate systems using Agrol® polyols. Nikki works closely with the Agrol® development team in testing new products for rigid foams.