Increasing the Solubility of Pentane in Rigid Foam Systems

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SUMMARY

Polyurethane rigid foams have been obtained using for a long time CFC 11 as blowing agent because the characteristics of this product seemed to be well tailored for PU foam, especially regarding physical properties, lambda value and solubility in raw materials.

Since 1995 it cannot be used because of its evident responsibility in the reduction of the ozone layer.

CFC 11 has been easily substituted by HCFC 141b, presenting this product very similar characteristics to CFC 11, i.e. good solubility in Raw Materials and good lambda value.

With HCFC 141 b we can have completely formulated polyols which, reacting with isocyanate, are quite useful to obtain a wide range of rigid foam.

Nevertheless its use is scheduled to be reduced in a few years, according to the last revision of the Montreal Protocol on ozone depleting substances, until the phase out scheduled in the first years of the 21 century because it continues to have some effect on ozone layer destruction.

The research has been involved to develop a product with no effect on the ozone layer, ecologically friend and easy to process in the rigid polyurethane foam technology.

Research developed pentane (normal, iso and cyclo-pentane) as blowing agent.

The characteristics of pentane comparing to CFC 11 and HCFC 141 b are listed in **Table 1**.

Generally speaking we could say that the pentane (C5) family presents worse lambda values comparing to CFC 11 and HCFC 141 b; that the flammability is very high, and that the solubility in polyols is very low.

Nevertheless all most important Companies producing panels via Double Band Lamination (DBL), and the appliance industry in Europe switched to C5 for ecological reasons.

Table 1. General characteristics of different blowing agents

Product	n-Pentane	i-Pentane	c-Pentane	HCFC 141B	CFC 11
Molecular weight	72	72	70	117	137
Boiling point, °C	36	28	50	32	24
Explosion limit, vol.%	1.4–8.0	1.4–7.6	1.5–8.7	5.6–17.6	None
Lambda vapour, W m°K	0.015	0.014	0.012	0.010	0.009
Solubility in polyols, pphp	5–10	5–10	10–20	50–100	50–100

INTRODUCTION

The substitution of CFC 11 or HCFC 141 b by pentane in PU rigid foam production, has determined the necessity to develop new products and new machines to obtain stable emulsions polyols/pentane.

To achieve this, the research was involved in testing new polyols, new silicone surfactants, new emulsifying additives and in the formulation optimisation by using new emulsion systems.

All most important companies involved in PU raw material production developed new products (mainly new polyols and new silicone surfactants) to obtain better performance in production: meanwhile also most important machines producer Companies developed new systems for an easy and safe handling of pentane.

Industry and machine producers have also studied and developed safety devices to feed, meter and emulsify pentane into the polyurethane systems.

These devices utilise the emulsion technology (because of low solubility of C5 family), to add the requested quantity of C5 in the polyol stream by means of static or dynamic mixers.

This seems to be the most attractive way and is the widely used technology in lamination panels production, in refrigeration panels and in appliance industry.

Nevertheless the low solubility of C5 is until now a big problem; the emulsions C5/polyols have not an high stability, they have difficulties to be controlled and give processing problems because of the difficulty to maintain a stable emulsion.

This effect is well known in lamination, where unstable emulsions yield to a bad cellular structure, to open cells, to loss of C5 ; this must be often overcome only reducing the amount of C5 with a consequent increase of the density.

This is well known also in appliances where, using in production the "day tank", (a tank where the requested pentane is added to the polyol component), often there are problems of phase separation at low temperatures, or for long period of stand by during the nights and the weekends.

This phase separation can occur also in the pipes of the plant giving a lot of problems each time at the beginning of the production.

To avoid the problem, all pipes should be cleaned and refilled, and all the polyol-containing pentane should be re-emulsified.

PURPOSE

The aim of this paper is to present a way to obtain a completely homogeneous blend of pentane in polyols.

The purpose of the research was to have a solution and not an emulsion, in order to maintain the stability of the blend for a long period of time.

This kind of blend permits to work in the same way we worked with CFC 11 in the past, and with HCFC 141 b until now.

These homogeneous solutions pentane/polyol components , are obtained using a special product soluble in pentane and in a wide variety of commune polyols for rigid foams, which acts as a vehicle to introduce more pentane in the polyol component.

EXPERIMENTAL

The research involved a wide number of interesting products, between them the best characteristics regarding the "solution effect" of the pentane in polyols, were found in the following product.

This product is named Kytane 20 A.S. ; and presents the following technical characteristics:

Formula: proprietary blend of alcanolamides

aspect	amber liquid
OH number	420±120 (mg·KOH/ g)
flammability point	more than 150°C
Viscosity at 25°C	1.100±100mPa·s
Specific gravity at 24/24°C	0.980±10.020

Because of its high OH number, this product does not affect the final characteristics of the foam and shows interesting processing properties, like the capability to increase the reactivity of the system and to reduce the amount of silicon surfactant.

For a good comprehension of how Kytane 20 A.S. works, and of its field of applications, it can be seen in the following tables some examples of formulation for a variety of applications , among which the continuous lamination panels production, the discontinuous panels production and the appliances production.

These formulations are based on different polyols widely used in Europe.

These examples show of course only a restricted application of Kytane 20 A.S: you have to consider that we obtained good solubility of pentane in almost all the polyols we tested even in lot of other trials not mentioned in this paper.

All the formulation reported have been tested in laboratory via hand mix: the first results in industrial trials are strictly reproducing the same characteristics we obtained in laboratory test.

Generally speaking we can affirm that increasing the amount of Kytane in polyol we can also increase the amount of pentane in solution; this solubilising effect is clearly demonstrated also if using only a small amount of Kytane.

The ratio between the amount of Kytane and the amount of pentane in solution is, in parts by weight:

100:100 for cyclopentane

100:50 for normal-pentane or isopentane

That means, for example, that adding 20 parts by weight of Kytane in a common formulation for appliance, we can have 20 parts by weight of cyclopentane completely soluble in the same formulation, or, alternatively, 10 parts by weight of normal-pentane or iso-pentane.

The final polyol components are completely homogeneous and normally keep their stability for a long time also at low storage temperature; these final "B" components can be easily emulsified with more pentane if you need lower density foams.

We report in the following 8 Tables examples of different formulations for rigid foam: Double Band Lamination, discontinuous panels production and domestic appliance.

All these formulations contain pentane, so their appropriate handling because of the flammability characteristics, and safety procedures must be the same adopted with pure pentane.

EXAMPLE 1 DBL PRODUCTION

Formulation for panels production via DBL, based on Caradol® LP 530.03, aromatic polyol by Shell Chemical.

CARADOL® LP 530.03	80.00
KYTANE 20 A.S.	20.00
WATER	3.00
L.6900*	1.00
CATALYST	2.00
FLAME RETARDANT	30.00
normal PENTANE	10.00
Parts by weight	146.00

* Osi Specialties Silicone Surfactant

This blend is completely homogeneous, stable and has not phase separation until 0°C

Viscosity at 25°C	= 200 mPa·s
Specific gravity at 24/24°C	= 1.040
CRUDE MDI (110 index), pbw	= 182.00

Reaction characteristics by hand mix at 25°C

cream time	12"
gel time	36"
free rise density	31.4 Kg/mc

FOAM CHARACTERISTICS

Dimensional stability:

24 hours at 100°C	linear variation	= +2.1 %
24 hours at –20°C	" "	= –0.7 %

Flame characteristics: (Numerical flame spread ratings of fire classifications are not intended to reflect hazards presented by this or any other material under actual fire conditions).

UNI 8457	category 2°
DIN 4102	class B3

Thermal conductivity (initial at 10°C) = 0.0249 W/m°K

Our experience in this field (we produce some million of square meters per year of continuous laminating panels with flexible facings with foam blown with n-pentane), confirms that the use of kythane 20 A.S. represents a good way to reduce problems in processing, when you use high quantity of pentane for low density foam.

We have had a drastic reduction of coarse cell formation: the mixing is always good and now we can introduce more pentane in our formulation than we used formerly, with reduction of water level, lambda value and costs.

EXAMPLE 2 DBL PRODUCTION

Formulation quite similar to the previous one, with an enhanced quantity of normal-pentane in solution.

CARADOL® LP 530.0	60.00
KYTANE 20 A.S.	40.00
GLYCEROL	10.00
WATER	1.00
L.6900*	1.00
CATALYST	2.00
FLAME RETARDANT	30.00
normal PENTANE	20.00
parts by weight	164.00

*Osi Specialties Silicone Surfactant

This blend is completely homogeneous, stable and has not phase separation until +10°C.

Viscosity at 25°C = 80 mPa·s

Specific gravity at 24/24°C = 0.990

CRUDE MDI (115 index) pbw 200.00

Reaction characteristics by hand mix at 25°C:

cream time	15"
gel time	39"
free rise density	31.6 Kg/mc

FOAM CHARACTERISTICS

Dimensional stability:

24 hours at 100°C:	linear variation = +2.4 %
24 hours at -20°C:	linear variation = -1.9 %

Flame characteristics: (Numerical flame spread ratings of fire classifications are not intended to reflect hazards presented by this or any other material under actual fire conditions).

UNI 8457	category 2°
DIN 4102	class B3

Thermal conductivity (initial at 10°C) = 0.0237 W/m°K

EXAMPLE 3 DISCONTINUOUS PANELS PRODUCTION

Formulation for discontinuous panels production based on Arcol® 3750, aromatic polyol by Arco Chemical:

ARCOL® 3750	80.00
KYTANE 20 A.S.	20.00
WATER	3.00
L.6900*	2.00
CATALYST	0.80
FLAME RETARDANT	30.00
normal PENTANE	10.00
parts by weight	145.80

* Osi Specialties Silicone Surfactant

This blend is completely homogeneous, stable and has not phase separation until +10°C.

Viscosity at 25°C = 250 mPa.s

Specific gravity at 24/24°C = 1.050

CRUDE MDI (120 index) pbw 205.00

Reaction characteristics by hand mix: at 25°C

cream time	22"
gel time	106"
free rise density	29.2 Kg/mc.

FOAM CHARACTERISTICS

Dimensional Stability:

24 hour at +100°C : linear variation = +2.2 %

24 hour at -20°C : " " = -0.8 %

Flame characteristics: (Numerical flame spread ratings of fire classifications are not intended to reflect hazards presented by this or any other material under actual fire conditions).

UNI 8457	category 2°
DIN 4102	Class B3

Thermal Conductivity (initial at 10°C) = 0.0238 W/m°K.

EXAMPLE 4 DISCONTINUOUS PANELS PRODUCTION

Formulation for discontinuous panel production with enhanced characteristics of flame retardancy, based on Ixol® B 251, flame retardant polyol by Solway S.A.

IXOL® B 251	60.00
KYTANE 20 A.S.	40.00
GLYCEROL	10.00
WATER	2.00
DABCO® D.C 193*	2.00
CATALYST	1.20
FLAME RETARDANT	30.00
normal PENTANE	20.00
parts by weight	165.20

*Air Products Silicone Surfactant

This blend is completely homogeneous, stable and has not phase separation until +10°C.

Viscosity at 25°C = 170 mPa·s

Specific gravity at 24/24°C = 1.130

CRUDE MDI (110 index), pbw = 183.00

Reaction characteristics by hand mix: at 25°C.

cream time	25"
gel time	122"
free rise density	29.8 Kg/mc

FOAM CHARACTERISTICS

Dimensional stability

24 hours at 100°C linear variation = +1.8 %

24 hours at –20°C: linear variation = –0.6 %

Flame characteristics (Numerical flame spread ratings of fire classifications are not intended to reflect hazards presented by this or any other material under actual fire conditions).

UNI 8457	Category 1°
DIN 4102	Class B2

Thermal conductivity (initial at 10°C) = 0.0240 W/m°K

EXAMPLE 5 POLYISOCYANURATE (PIR) PRODUCTION

Formulation for production of panels in PIR, based on Isoexter® 3153, aromatic polyester by Coim SpA.

ISOEXTER® 3153	50.00
KYTANE 20 A.S.	50.00
DABCO® D.C. 193*	2.00
CATALYST	2.50
FLAME RETARDANT	30.00
normal PENTANE	30.00
parts by weight	164.50

* Air Products Silicone Surfactant

This blend is not homogeneous, and in some hours separation of phase occurs because of the very low compatibility of this polyester polyol with pentane; meanwhile the compatibility of normal-pentane in this blend is increased a lot and the process is quite easy and good.

Viscosity at 25°C = 90 mPa·sec

Specific Gravity at 24/24°C = 0.990

CRUDE MDI (300 index) pbw = 300.00

Reaction characteristics by hand mix at 25°C:

cream time	15"
gel time	48"
free rise density	28.4 Kg/mc

FOAM CHARACTERISTICS

Dimensional stability:

24 hours at 100°C linear variation = +0.8%

24 hours at –20°C linear variation = –0.4 %

Flame characteristics: (Numerical flame spread ratings of fire classifications are not intended to reflect hazards presented by this or any other material under actual fire conditions).

UNI 8457	Category 1°
DIN 4102	Class B2

Thermal conductivity (initial at 10°C) = 0.0244 W/m°K

EXAMPLE 6 POLYISOCYANURATE (PIR) PRODUCTION

Formulation for panels production in PIR, based on Stepanpol® PS 3152, polyester polyol by Stepan Ltd.

STEPANPOL® PS 3152	50.00
KYTANE 20 A.S.	50.00
DABCO® D.C. 193*	2.00
CATALYST	3.00
FLAME RETARDANT	30.00
normal PENTANE	30.00
parts by weight	165.00

* Air Products Silicone Surfactant

This blend is not homogeneous, and in some hours separation of phase occurs; meanwhile the compatibility of normal-pentane in this blend is a lot increased and the process is quite easy and good.

Viscosity at 25°C	= 85 mPa·sec
Specific gravity at 24/24°C	= 0.990

CRUDE MDI (300 index) pbw = 288.00

Reaction characteristics by hand mix at 25°C:

cream time	= 14"
gel time	= 38"
free rise density	= 28.9 Kg/mc

FOAM CHARACTERISTICS

Dimensional stability

24 hours at 100°C linear variation	= +1.5 %
24 hours at −20°C linear variation	= −1.0 %

Flame characteristics (numerical flame spread ratings of fire classifications are not intended to reflect hazards presented by this or any other material under actual fire conditions).

UNI 8457	Category 1°
DIN 4102	Class B2

Thermal conductivity (initial at 10°C) = 0.0239 W/m°K

EXAMPLE 7 APPLIANCE FORMULATION

Formulation for appliance production based on Voranol® RN 411, Dow Chemical polyether polyol.

VORANOL® RN 411	80.00
KYTANE 20 A.S.	20.00
WATER	2.00
L.6900*	1.00
CATALYST	2.00
normal PENTANE	10.00
parts by weight	115.00

* Osi Specialties Silicone Surfactant

This blend is completely homogeneous, stable and has not phase separation until 0°C.

Viscosity at 25°C	= 420 mPa/sec
Specific gravity at 24/24°C	= 1.010

CRUDE MDI (105 index) pbw = 136.00

Reaction characteristics by hand mix at 25°C

cream time	= 14"
gel time	= 52"
free rise density	= 26.3 Kg/mc

FOAM CHARACTERISTICS

Dimensional stability:

24 hours at 100°C linear variation	= +1.8 %
24 hours at −20°C linear variation	= −0.8 %

Thermal conductivity (initial at 10°C) = 0.0247 W/m°K

NOTE 1: It is important to say that this formulation is normal-pentane based for appliance, with a very good foam with low cost and good lambda value.

Better lambda values can be obtained by using cyclo-pentane instead of normal-pentane as in following example.

EXAMPLE 8 APPLIANCE FORMULATION

Formulation for appliance production based on Arcol® 3544, Arco chemical polyether polyol.

ARCOL® 3544	80.00
KYTANE 20 A.S.	20.00
WATER	1.00
L.6900*	1.00
CATALYST	2.00
cyclo-PENTANE	20.00
parts by weight	124.00

* Osi Specialties Silicone Surfactant

This blend is completely homogeneous, stable and has not phase separation until 0°C.

Viscosity at 25°C	= 230 mPa/sec
Specific Gravity at 24/24°C	= 0.990

CRUDE MDI (105 index) pbw = 136.00

Reaction characteristics by hand mix at 25°C:

cream time	20"
gel time	60"
free rise density	23.9 Kg/mc

FOAM CHARACTERISTICS

Dimensional stability:

24 hours at 100°C linear variation	= +2.2 %
24 hours at –20°C linear variation	= –1.1 %

Thermal conductivity (initial at 10°C) = 0.0249 W/m°K*

FINAL CONSIDERATIONS ON APPLIANCE

The formulations presented with high quantity of pentane completely soluble in polyol component, show outstanding advantages comparing to a standard formulation cyclo-pentane based as today widely used:

Lower use of water (exothermic reduction, better adhesion)
Crude MDI lower consumption (cost reduction)
Higher use of cyclopentane (better lambda value)
Easy substitution of cyclopentane with normal pentane

CONCLUSION

Polyurethane rigid foams have been obtained for a long time by using as blowing agents CFC 11 and HCFC 141 b in complete solution in Polyol Component (or "B" Component).

Nowadays the widely used PU systems for insulation in appliance, refrigeration industry panels, and continuous laminating panels, are using for ecological reason pentane, (normal, iso or cyclo-pentane), as blowing agent, even if pentane is known to have some problem in solubility and in processing.

**In our experience we may consider this lambda value, at very low density and hand mix, corresponding to a value of about 0.0229 W/m°K at moulded density of about 30–35 kg/mc, with machine mixing.*

Kytane 20 A.S. widely increases the solubility of pentane in most of the commonly used Polyols, obtaining completely homogeneous systems, easy to process and with good final foam characteristics.

ACKNOWLEDGEMENT

I would like to thank Mr. G. Cini of Dow Benelux N.V., for his help in producing this paper.

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BIOGRAPHICAL NOTE

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Dr. C. Chittolini received his degree in organic chemistry from the University of Modena, Italy in 1970. He worked since 1973 in different companies involved in production of PU systems for rigid and flexible foams, and in elastomers. In 1990 he joined Ediltec as a Technical Manager responsible for Quality Assurance.