

The influence of isomer composition and functionality on the final properties of aromatic polyurea spray coatings

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Abstract

The chemical reaction to form a polyurea is very fast and not sensitive to humidity and low temperature. Consequently, polyurea coatings can still be used in climatic conditions where conventional coating systems fail owing to, for example, their sensitivity to water or very slow curing rate.

Typically a polyurea formulation comprises a liquid MDI-based modified quasi-prepolymer with a NCO-content of 16% together with a combination of polyoxyalkylene di- and/or triamines with diethyltoluene diamine. Such systems have very short gel times and are thus difficult to apply.

The spray equipment required to apply such coatings must therefore be designed to ensure quick and efficient mixing of the components. It is, however, preferable to keep the mixing ratio at 1:1 in volume and the viscosity of the two components similar. The index of the system is usually kept at approximately 1.05.

To assist their use the properties of these systems can be modified in a number of ways. Adding propylene carbonate improves the flow and wetting properties; it also reduces the reactivity of a system. Modifying the mixed MDI isomer composition to give higher 2,4'-isomer content gives longer gel times. The use of sterically-hindered diamines has a significant impact on the cure time as well.

In this paper, the effects of specific parameters on the final properties of polyurea spray coatings are reported, specifically: the influence of varying the mixed isomer composition on the cure speed and film properties; the influence of slow-reacting reagents on the film properties; and the influence of the functionality of the isocyanate prepolymer and the resin blend on cure speed, cure efficiency and film properties.

Introduction

Polyurea chemistry is based upon the reaction between isocyanates and primary or secondary amines to form urea groups (Fig.1). The isocyanate component is a soft block prepolymer based on MDI and polyether polyols. Polyether amines may also be used as the soft block in the prepolymer, but owing to the high reactivity careful high-pressure mixing is necessary. The amine component, which is also referred to as the resin blend, is a polyether amine and a chain extender (e.g. diethyltoluene diamine (DETDA), dimethylthiotoluene diamine (DMTDA), and/or secondary diphenylmethane diamine).

Figure 1: Basic structure of polyurethane and polyurea

Polyurethane	Polyurea
RNH-CO-O-R'	RNH-CO-NH-R'

The isocyanate/amine reaction is extremely fast, with gel times less than 3 seconds. Because there is no catalyst required, the reliability of the reaction mechanism is very good. At such high reaction speeds it is preferable if a mixing ratio of 1:1 is used and that the viscosities of the two components are about the same to ensure efficient mixing.

The advantages of polyurea spray elastomers are that 100% solids are applied (i.e. there are no volatile components, solvents or water, for example), they are catalyst-free, have high reactivity, and exhibit excellent mechanical properties and chemical resistance.

Experimental programme

An experimental programme to assess the effects of specific parameters on the reaction and final properties of polyurea spray coatings was carried out in two parts. In the first part, a study was undertaken of the influence of the functionality (Fn) of the MDI prepolymer and of the resin blend on the application and film properties. In the second part, the influence of the 2,4'-isomer content on the film properties was examined.

1. Experimental parameters

1.1. Influence of functionality

The MDI prepolymers used in this study have an increasing functionality, resulting in increasing density and viscosity. The viscosity is an important, limiting property because the two components have to be mixed in a very short period. Selected properties of the prepolymers used for this part of the study are shown in Table 1.

Table 1: Properties of prepolymers used to test influence of functionality

	Product name	% NCO
USA	RUBINATE [®] 9009	15.8
	RUBINATE [®] 9480	15.5
	RUBINATE [®] 9495	15.2
	RUBINATE [®] 9484	15.8
Europe	Experimental product EID 9211 (equivalent to RUBINATE [®] 9480)	15.5
	Experimental product EID 9212 (equivalent to RUBINATE [®] 9495)	15.2
	SUPRASEC [®] 2054	15.0
	SUPRASEC [®] 2045	16.0

* rd = reactive diluent, not considered as VOC

The resin blends used in the study are shown in Table 2. They have been formulated such that blends 1 and 2 are fast-reacting, while blend 3 is slow-reacting.

The systems are calculated to have an index of 1.05 at a 1:1 volume mixing ratio.

Table 2: Composition of resin blends used to test influence of functionality

Code	Composition	Quantities	Fn
Blend 1	JEFFAMINE [®] D 2000/DETDA	73.5/26.5	2.00
Blend 2	JEFFAMINE [®] T 3000/DETDA	73.5/26.5	2.14
Blend 3	JEFFAMINE [®] T 3000/UNILINK [®] 4200	50.3/49.7	2.09

1.2. Influence of 2,4'-isomer content

The properties of the MDI prepolymers used to study the influence of the 2,4'-isomer content are shown in Table 3. They contain an increasing 2,4'-isomer content, which results in an increasing viscosity. ISO 7 contains a plasticiser, which explains its lower viscosity, while ISO 10 is a slightly modified version of ISO 9, which results also in a higher viscosity.

Table 3: Properties of isocyanates used to test influence of 2,4'-isomer content

Code	Conc. 2,4' (%)	Fn	Viscosity, mPas	
			25°C	65°C
ISO 6	25	low	670	80
ISO 7 ¹	30	low	550	70 ¹
ISO 8	40	low	900	110
ISO 9	50	low	950	110
ISO 10	50	low ²	1200	135

¹ contains plasticiser

The composition of the resin blend used is shown in Table 4.

Table 4: Composition of resin blend used to test influence of 2,4'-isomer content

Composition	Ratio (w/w)	Viscosity at 25°C, mPas	Fn
JEFFAMINE [®] D 2000/ JEFFAMINE [®] T 5000/ DETDA	26/40/34	950	2.04

1.3. Spray application

In the first series of tests (to examine the influence of functionality), the isocyanate component used was diluted with 10% reactive diluent. In the second series of tests (to examine the influence of the 2,4'-isomer content) the isocyanate component was not diluted.

All applications of the coatings were carried out at an index of 1.00 - 1.05 and an application temperature of 75°C.

In the first series of tests the application pressure was 160 bar; in the second series it was 180 bar.

The thickness of the cured film varied from 700 to 2000 microns.

1.4. Conditioning

In all the tests, the systems were applied on a stainless steel panel that had been pre-treated with a release agent. The films were conditioned for ten days at 23°C and 50% relative humidity prior to testing.

2. Test results

2.1. Effect of viscosity

The viscosity of the components has an important influence on how easy it is to spray-apply the system. At higher viscosities, the equipment suffers more. For example, the viscosity of the MDI prepolymer with the highest functionality (ISO 5), was still 110 mPas at 75°C after a 10% dilution (Table 5). This was too high for the pumps on the equipment.

Table 5: Influence of temperature and dilution on viscosity of isocyanate

Temperature, °C	Viscosity, mPas (ISO 5, highest Fn)		
	100%	+ 10% rd*	+20 % rd*
25	5600	3300	1400
70	260	140	80
75	230	110	65
80	190	100	55
85	160	80	50

* rd = reactive diluent, not considered as VOC

However, a more important reason for keeping the viscosity low is the mixing efficiency. For application by spray gun, the products have to be mixed in a very short time in a small mixing chamber. If the viscosity of the MDI prepolymer is too high, or if the difference in viscosity between the MDI prepolymer and the resin blend is too great, mixing becomes inefficient. This results, in extreme cases, in visual defects in the film.

For spray application it is necessary for the viscosity to be below 100 mPas and, preferably, around 50 mPas at application temperature if possible.

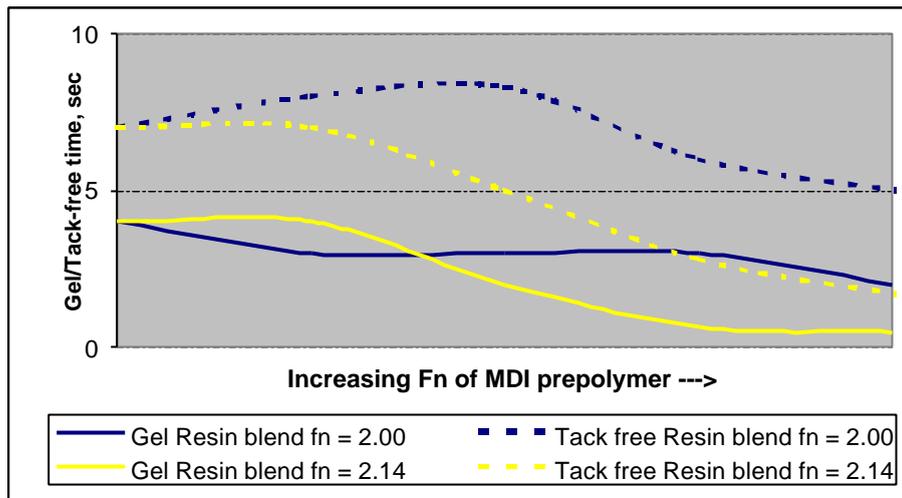
2.2. Effect of functionality

To measure the effects of increasing functionality, several different properties were examined.

2.2.1. Gel time, tack-free time

Reactivity is strongly affected by the increasing functionality of the MDI prepolymer. As this functionality increases the tack-free time decreases faster than the gel time. Consequently, the functionality of the resin blend becomes influential and more significant as the functionality of the MDI prepolymer increases (Figure 2).

Figure 2: Effect of functionality on gel time and tack-free time

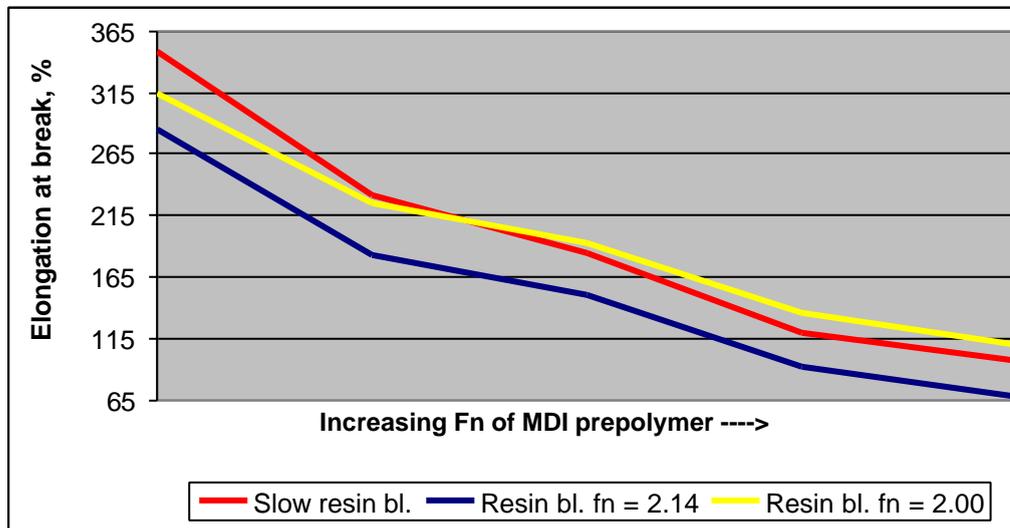


2.2.2. Elongation at break

The elongation at break drops, logically, as the functionality of the MDI prepolymer increases. This is shown in Figure 3. The slow-reacting resin blend (initially the top plot), has a higher elongation at break for low-functionality MDI-prepolymers but becomes lower at medium functionality.

The elongation was measured according to DIN 53504.

Figure 3: Effect of functionality on elongation at break



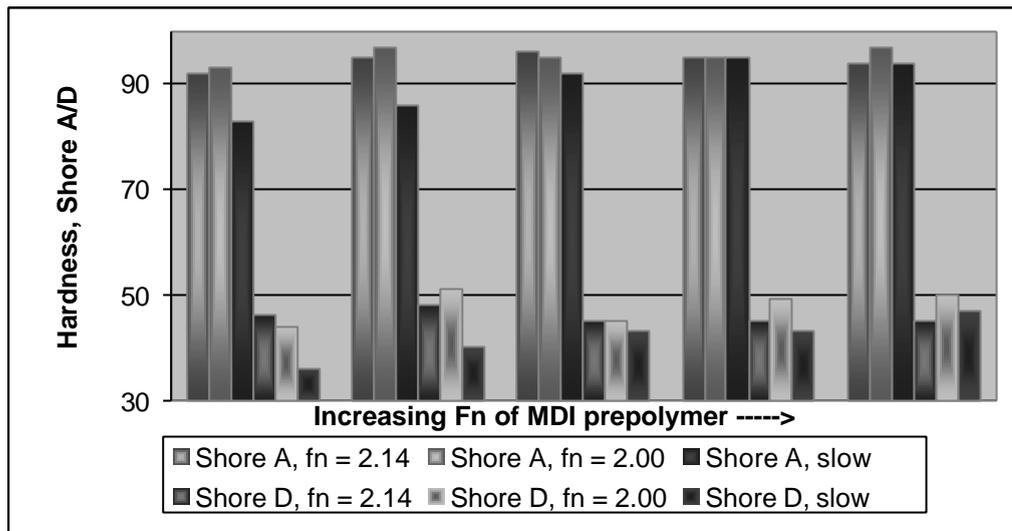
2.2.3. Shore hardness

The measured values for Shore hardness (A or D) are very similar for the two highly-reactive resin blends (Figure 4) and are not influenced by the functionality. The increase in hardness that might be expected for higher functionality MDI prepolymers is probably lost because of the lower cross-linking efficiency.

For the slow-reacting resin blend, however, there is an increase in hardness.

The film hardness was measured according to DIN 53505.

Figure 4: Effect of functionality on film hardness



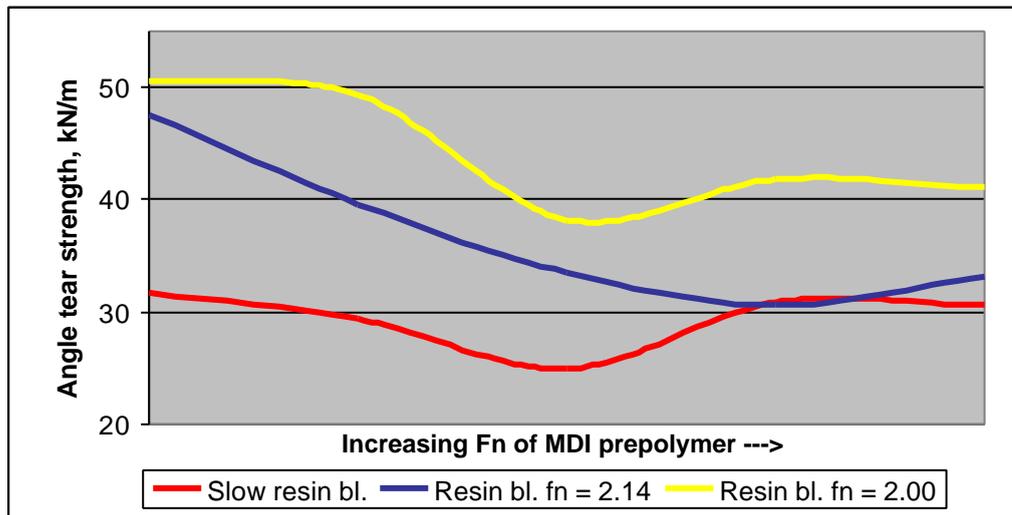
2.2.4. Angle tear strength

Investigation of the angle tear strength shows that although the functionality of the MDI prepolymer increases, the angle tear strength decreases (Figure 5). This is probably because the cross-linking efficiency drops. Beyond a point, however, the higher functionality compensates partially for the loss in cross-linking efficiency.

The results obtained for the slow-reacting resin blend, show a profile that is similar to that for the di-functional resin blend but with much lower values, which indicates that the conversion is dropping.

The angle tear was measured according to DIN 53515.

Figure 5: Effect of functionality on angle tear strength

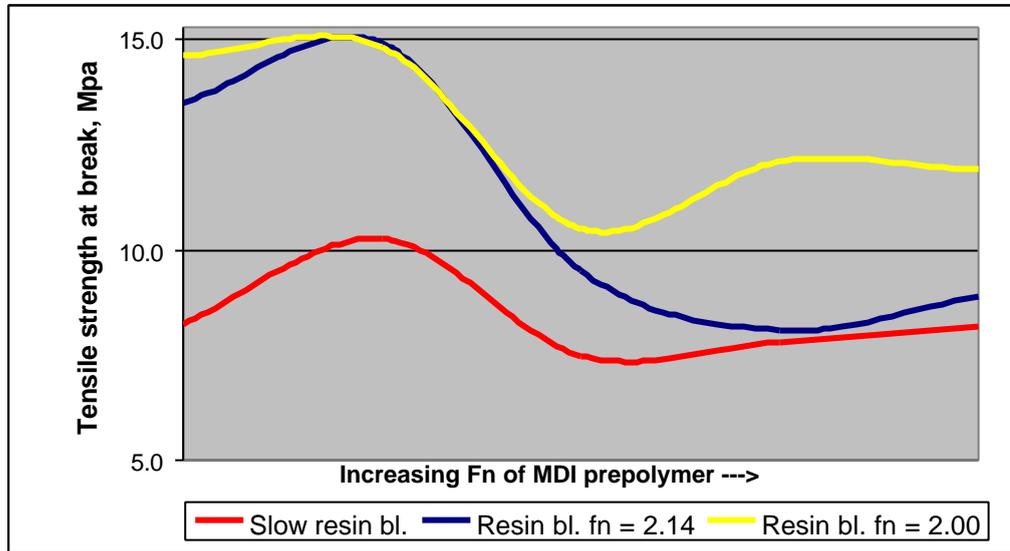


2.2.5. Tensile strength

The results obtained in tests on tensile strength show similar profiles to those obtained when measuring the angle tear, as illustrated in Figure 6.

Tensile strength was measured according to DIN 53504.

Figure 6: Effect of functionality on tensile strength

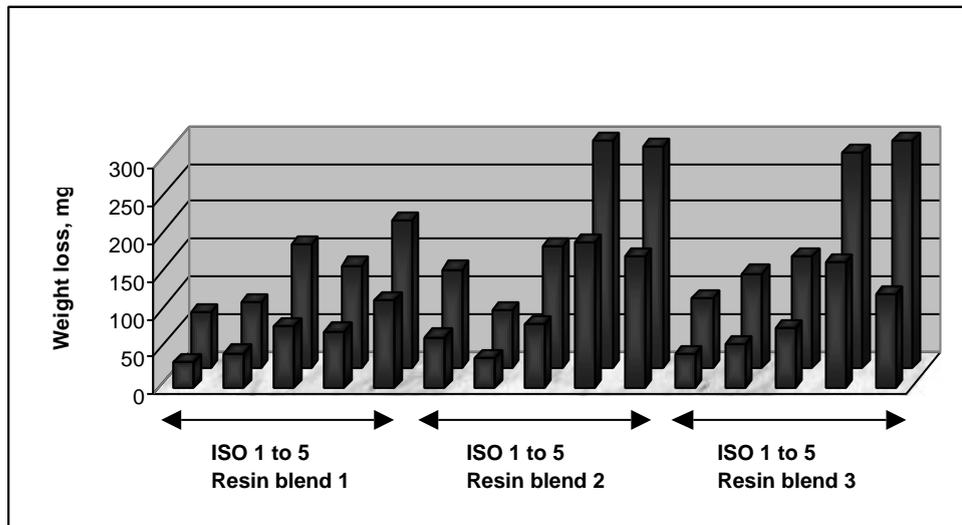


2.2.6. Taber abrasion resistance

The abrasion resistance of the films produced was tested according to ASTM D 4060 for 500 & 1000 cycles using H18 abrasive wheels and a weight load of 500 g. The results obtained using isocyanates 1 to 5 with resin blends of different functionality are shown in Figure 7. In the first 5 systems shown the functionality of the resin blend was 2.00, in the middle 5 systems it was 2.14 and in the last 5 systems the slow-reacting resin blend was used.

For all three resin blends, the lower functionality MDI prepolymer gave the lowest weight loss.

Figure 7: Influence of functionality on film abrasion resistance



2.2.7. Chemical resistance

The chemical resistance of the films produced was measured by an immersion test performed according to ASTM D1308, under which the film was immersed for periods of 1 hour and 1 day at 23°C. Resistance to methanol, acetone, xylene, hexane, brake fluid, diesel fuel, petrol, ethylene glycol were tested.

The results obtained showed that chemical resistance decreases as the functionality increases. The slow-reacting resin blend gave the worse results, but is less influenced by an increase in the functionality.

2.3. Effect of 2,4'-isomer content

The advantages of a higher 2,4'-isomer content are lower reactivity and longer gel times (from 3 seconds to 5 - 6 seconds). Although the differences in gel times are comparatively small, they have a significant influence on the flow properties of the system, making the difference between poor and good flow.

An increase in the 2,4'-isomer content results in a decrease in the hardness and significantly decreases the tensile strength and angle tear (Table 6).

The MDI prepolymer ISO 10, a modified version of ISO 9, gives physical properties that are comparable to those obtained with variants which have a low 2,4'-isomer content whilst keeping the benefits gained by using variants with a high 2,4'-isomer content.

Table 6: Influence of 2,4'-isomer content on film properties

Code	Gel/Tack-free time	Shore A	Shore D	Tensile strength, MPa	Angle Tear, strength kN/m
ISO 6	3 sec/ 6 sec	97	54	9.2	95
ISO 7	4 sec/6 sec	99	55	9.3	85
ISO 8	5 sec/7 sec	97	52	8.2	62
ISO 9	6 sec/8 sec	93	52	7.4	63
ISO 10	6 sec/8 sec	96	53	10.3	81

Discussion

Following the experimental programme, the effects of functionality and of higher 2,4'-isomer content on polyurea spray coatings are summarised below.

1. Effects of functionality

Because of the high reactivity of the systems, it is difficult to determine the gel time/tack-free time accurately, as suitable measuring equipment is not commercially available. The reliability of the measurements is strongly dependent on the expertise of the operator. Nevertheless, it was noticed that the reaction became faster as the functionality of the MDI prepolymer increased. At higher functionality, the reduction in the tack-free time is quicker than the reduction in the gel time.

Also, when the functionality of the MDI prepolymer is high, the functionality of the resin blend has more influence on the reactivity of the system.

The elongation decreases, as expected, with increasing functionality. However, the behaviour is not linear.

The influence of the functionality of the MDI prepolymer on the Shore hardness is minimal for the highly-reactive systems. For the slow-reacting resin blend, however, there is an increase in hardness with increasing functionality.

The functionality-dependent performance profiles of angle tear and tensile strength behave similarly. As the functionality of the system increases, angle tear and tensile strength decrease because the efficiency of cross-linking is reduced. But with a higher MDI prepolymer functionality, the angle tear and tensile strength increase again because the higher functionality compensates somewhat for the loss in cross-linking efficiency. Comparing the two highly-reactive resin blends, the one with the higher functionality gives lower angle tear and tensile strength than the di-functional resin blend, which has a lower functionality.

The fact that for the slow-reacting resin blend the values are still lower might indicate that the conversion of sterically-hindered or secondary amines is lower. The non-reacted part behaves as a plasticiser.

The decrease in cross-linking efficiency is confirmed by the abrasion test. The weight loss increases with the increasing functionality of both the MDI prepolymer and the resin blend.

This behaviour is again confirmed by the chemical resistance test; the resistance decreases with increasing functionality.

2. Effects of 2,4'-isomer content

The use of higher 2,4'-isomer containing MDI prepolymers has the advantage that it gives longer gel times, which results in less critical application conditions and a better finish. The applied coating has, in the end, a better flow.

Increasing the 2,4'-isomer content necessitates working with products that have a higher viscosity. The viscosity can be adjusted by diluting the MDI prepolymer with a (preferably) non-VOC-containing and possibly reactive diluent.

An increased 2,4'-isomer content also has a negative effect on the physical properties of the cured film. While the hardness of the coating remains the same, the tensile strength and angle are reduced. By modifying the MDI prepolymer (ISO 10), it was possible to maintain the slower reactivity and to improve the physical properties such that they were similar to those obtained using MDI prepolymers with a low 2,4'-isomer content.

Conclusions

Optimum film properties are obtained when MDI prepolymers with low functionality are used. Although it was expected that properties such as chemical resistance, angle tear and tensile strength would improve because of a higher cross-linking density, the test results showed inferior properties when MDI prepolymers with medium to high functionality are used. This is caused by the higher reactivity, which gives a faster increase in viscosity and immobilisation of the polymer network, combined with the higher viscosity of the MDI prepolymer, which gives a less effective mixing of the two components during application.

MDI prepolymers with higher 2,4'-isomer content give longer gel times but this has an influence on the viscosity of the MDI-prepolymer and the physical properties of the cured film. By modifying the application conditions and/or the use of a non-VOC, reactive diluent, the viscosity can be monitored. The physical properties can be corrected by slightly modifying the MDI prepolymer.

An overview of the MDI prepolymers that are available from Huntsman Polyurethanes for these applications is given in Table 7.

Table 7: MDI prepolymers from Huntsman Polyurethanes for polyurea spray coatings

	Product name	% NCO
USA	RUBINATE [®] 9009	15.8
	RUBINATE [®] 9480	15.5
	RUBINATE [®] 9495	15.2
	RUBINATE [®] 9484	15.8
Europe	Experimental product EID 9211 <i>(equivalent to RUBINATE[®] 9480)</i>	15.5
	Experimental product EID 9212 <i>(equivalent to RUBINATE[®] 9495)</i>	15.2
	SUPRASEC [®] 2054	15.0
	SUPRASEC [®] 2045	16.0

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