"Robust Polyurea Grease for Wide Range of Industrial Applications"

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Abstract:

Polyurea greases are known for their unusual high temperature capabilities. On the other hand, initial polyurea greases reported were associated with some disadvantages like poor shear stability, storage hardening, pumpability, limited rust and extreme pressure-antiwear characteristics. However significant amount of work has been reported to improve these greases. NLGI's latest grease market survey indicates that polyurea greases constitute about 4 % of the total worldwide grease volumes and are most popular greases in Japan constituting about 25 %. Contrarily, in countries like India this class of greases have not picked up significant volumes, probably because of manufacturing concerns.

Polyurea greases initially produced in our plant exhibited inferior mechanical stability and limited shelf life and therefore, there was a need to improve these greases so as to make them suitable for wide range of applications. In view of this, improved polyurea grease was developed which has demonstrated improved shear stability , better rust protection, outstanding extreme pressure properties. These interesting test results have been covered in this paper.

Introduction:

Urea compounds are perhaps one of the earliest known compounds and polyurea compounds were patented as early as in 1930's where their potential applications were probably other than for greases (1). Polyurea thickeners for formulating greases as ureido and amido compounds were reported in 1950's (2-4). This class of greases were claimed to possess good high temperature application capabilities. The reasons for their unusual high temperature capabilities may be attributed due to the property of polyurea greases to thicken with increase in temperatures whereas soap base greases, in general, tend to soften with increase in temperature. This unique property is expected to provide longer bearing life at high temperature. Additionally the longer life of polyurea greases may also be due to the fact that they contain no metal preventing their oxidation at elevated temperatures whereas in case of metal based soap greases, metal present in the thickener may catalyze the oxidation and thus reducing the service life of grease at high temperatures (5, 6). Another distinction of these greases over soap based greases is that the molecular structure of these greases is potentially dominated by hydrogen bonding whereas in the case of soap base greases bonding is primarily dominated by weaker Van der Waal forces (1). This might provide polyurea greases better structural stability at elevated temperatures and a preferred choice for fill for life applications over metallic based counterparts.

Various investigators reported different reactants and different reaction mechanism to synthesize urea thickeners for making greases viz., diureas, triureas, tetraureas and polyureas. The end use properties of resultant polyureas have been reported to be influenced to a large extent by the type of reactants as well as process parameters (4-5, 7-11). On the other hand, early polyurea greases were associated with some disadvantages like as poor shear stability, storage hardening, poor shelf life, limited rust protection, limited extreme pressure, anti-wear properties and poor pumpability etc. A considerable amount of work has been reported in the recent past to improve these properties so as to make them more viable for specific end user applications. With advancement in formulation technology to make them user friendly , these greases now find applications in different industries such as radiation resistant, water resistant, extreme pressure, corrosion resistant , electric contacts and even as food grade greases etc. (12-18). Because of wide range of applications and significant amount of research in this area, the volumes of these greases are steadily growing. NLGI's latest grease market survey indicates that polyurea greases constitute about 4 % of the total worldwide grease volumes whereas in North America it is about 5.7 %. Interestingly, polyurea greases are most favored in Japan, constituting about 25 % of the volume and their market share is growing (19).

Different polyureas indicate the involvement of different chemical compounds and thus invite a vast array of chemical reaction possibilities and ample opportunities for synthesizing novel polyurea compounds suitable as thickeners for greases with diverse properties. However, the challenge lies in synthesizing a suitable polyurea thickener where the inherent drawbacks associated with this class of greases as mentioned above can be minimized. In our endeavor to develop multi-purpose polyurea grease suitable for different applications, improved polyurea grease have been developed and evaluated in recent past. This grease exhibits improved shear stability, shelf life, better rust protection, extraordinary extreme pressure (620 kg weld load and 60 lbs Timken) properties besides retaining its inherent high temperature characteristics. These interesting test results have been covered in this paper. Additionally, shelf life, shear reversibility and compatibility data have also been covered in this paper.

Experimental:

The grease samples selected for these investigations were prepared either in the laboratory or were commercial plant samples**.** Samples prepared in the laboratory were prepared in open kettle and under atmospheric pressure conditions. To avoid many variances in these investigations composition and process parameters while preparing greases both in laboratory and commercial plant remained practically same. Greases produced in commercial plant comprise both open kettle and contractor process. The samples were tested as per the standard ASTM / IP methods. More relevant details about the grease samples will be covered under results and discussion.

Results and Discussion:

Characteristics of Conventional Polyurea Greases:

The term conventional polyurea greases referred herein are polyurea greases initially produced by our company. Two types of polyurea greases (Grease A and Grease B), both having different composition and application have been chosen for these studies. Grease A was basically intended for industrial applications and Grease B for automotive application. Both greases are based on mineral oil and performance additives were added to meet the performance requirement. Grease A is in NLGI 2 consistency and Grease B in NLGI 1.5 consistency. These greases, in general, are prepared with combination of substituted aliphatic amines and toluene diisocyanate (TDI); performance additives were added to match the desired specification. Typical physic-chemical and performance test data of both Grease A and Grease B are tabulated in table -1. Test data of Grease A indicate that grease consistency is NLGI 2 and has high drop point of 259 ^{0} C making this grease suitable for high temperature applications. The weld load of 400 kg and Timken OK load 50 lbs also indicates that this grease is suitable for extreme pressure and heavy duty applications. Grease B also exhibited similar characteristics except consistency in NLGI 1.5. Both the greases thus demonstrated high temperature and extreme pressure capabilities and satisfactory performance in the applications. However these greases exhibited inferior mechanical / shear stability (+ 50 unit change in penetration after 10,000 double strokes) and also poor shelf life which is the common characteristics of polyureas greases but may be considered disadvantage in applications where grease need to be pumped like one in case of centralized lubrication system.

For studying the shelf life of this type of greases, five retention samples namely Grease C, Grease D, Grease E, Grease F, grease G, which were of over more than 2 years old and were produced in commercial plant were taken and tested for penetration, drop point, mechanical stability . The samples more than above stated period were not available for studies. Test results are tabulated in table - 2 and data indicate that greases got hardened up significantly which is evident from the unworked penetration data. All the grease samples at the time of manufacture were in NLGI 2 (penetration 265-295) grade which settled over a period of more than 2 years to NLGI 3 (Unworked penetration) , however the work penetration data still found to close to softer side NLGI 2 consistency . Drop point of all the greases under study was more than 250 ^{0} C which found to be well within expected limits. The visual observation of samples delineated that there was some oil separation from the greases. Additionally, these greases have exhibited shear reversibility, settling with time as per penetration and mechanical stability test (figure-1 and figure 2). The hardening of greases as evident from unworked penetration and oil separation indicate that grease has poor shelf life and considered an application limitation of greases particularly in pumpability, in spite of the fact that there were no performance complaints as such. Additionally manufacturing grease from toluene diisocyanate (both 2,4- and 2,6- isomers) is always issue for the plant as toluene diisocyanate is considered highly toxic and serious health hazard.

Development and Characteristics of Improved Polyureas Greases:

The efforts to improve existing polyurea grease technology has been attributed mainly due to following two reasons

- Manufacturing concerns – handling of toxic ingredients
- Improving shelf life and performance

There has been growing concern for handling toxic raw materials in the plant and a need was felt to develop improved grease both in terms of quality and manufacturing ease . In view of this, systematic efforts have been made in our Riverside Laboratory to develop grease with improved properties. After concerted efforts improved grease thickener was developed and tailor made for different applications both for automotive and industrial applications. The properties of two finished greases Grease H and Grease I are described below. Grease H is intended for industrial applications and Grease I is slated for automotive applications including for constant velocity joints. Both the greases were made in mineral oil and VG 220 base oil viscosity

The physcio-chemical performance test data of Grease H and Grease I are enclosed in table -3. These data are compared with Grease A which was grease produced with old conventional process and materials. Table indicate that grease H and Grease I both exhibited improved high drop points of 277 ^{0} C and 275 ^{0} C compared to 259 of Grease A. Weld load of Grease A was 400 kg whereas both the greases (Grease H and Grease I) exhibited 620 kg which is considered very high and sufficient to cover any extreme pressure applications. Both Grease H and Grease I exhibited Timken OK load of 60 lbs compared to 50 lbs for Grease A which is again very high for heavy duty applications and thus indicating exceptionally high extreme pressure capabilities of both greases i.e., grease H and Grease I. Besides this, grease also possesses good water washout out characteristics. Additionally this grease also passes rust test tested (ASTM D 1743) and copper corrosion test, indicating good anti-rust and corrosion resistant properties.

Mechanical stability data of this grease indicate this grease is comparatively more shearing stable than previously made greases by us. Mechanical stability tested as per ASTM D 217 indicate about 30 unit change in 100,000 strokes which expected to be excellent for polyurea greases compared to 51 unit for Grease A .Additionally roll stability of Grease H and Grease I are 6.4 and 8.4 % respectively compared to 14.5 % for Grease A and thus indicating that this grease is stable compared to previously produced greases.

To further investigate versatility of the thickener system two more greases were prepared with same thickener (Grease J and Grease K) **.** Grease J was prepared in VG 460 base oil and in mineral oils whereas Grease K is based on synthetic oil and in VG 220 viscosity grade**.** Test data are tabulated in Table – 4. Grease L discussed in table is commercially available grease based on Synthetic oil and is for comparison purpose with Grease K. Grease J like Grease H has exhibited high drop point, high weld load and Timken OK load and exhibited good mechanical stability close to lithium type of greases. Grease K when compared with commercially available synthetic polyurea grease exhibited improved mechanical stability and extreme pressure characteristics. However to establish this observation comparison should have been made with more synthetic oil based polyurea greases and therefore this observation might have limited relevance.

Shear Reversibility:

Polyurea greases possess inherent shear reversibility which is described by the property by which grease softens with working or under stress and tries to regain its consistency when shear force is removed. The kind of shear reversibility behavior is also exhibited by aluminum complex and titanium complex greases (20). This unique property may possibly help long service life of grease particularly in stop and run conditions**.** The conventional grease as described above has indicated excellent shear reversibility characteristics (figure 1 and 2). Improved polyurea grease discussed above has demonstrated good mechanical and shear stability. This improved mechanical / shear stability may probably result into change in behavior of grease especially in shear reversibility characteristics. To study whether this improved polyurea grease as a resultant of change in composition has resulted in to similar shear reversibility behavior or else this property is compromised , the shear reversibility of these greases were also studied (figure 3 and 4). These figures indicate that these greases are still shear reversible but not to the extent as above mentioned conventional greases.

Compatibility with Lithium Complex and Ca-sulfonate Greases

Polyurea greases are generally considered incompatible with other greases and therefore not very user friendly in some industries. For OEM filled bearing there possibly could not be any issue but for service applications or else refilling, incompatibility becomes a concern. Besides this, there are applications like centralized lubrication systems where completely removing greases already in use or cleaning bearing becomes cumbersome and difficult, incompatibility of one grease with other greases could be a cause of serious concern.

As polyurea greases are expected to be used where possible change over could be either lithium complex or sulfonate complex greases, therefore these two type of greases were studied for compatibility with improved polyurea grease. Both these lithium complex and overbased calcium sulfonate complex greases taken for these studies are greases produced in commercial plant and are fortified with performance additives. For comparative study blends of old conventional polyurea grease were also made with lithium complex and calcium sulfonate complex grease. Lithium complex and calcium sulfonate greases are same as used in case of blends with improved polyurea greases. This was done to avoid any other variance in study and also to avoid effect of change of additives.

Compatibility test were conducted on the line with ASTM 6185 test protocol and was tested for primarily compatibility tests (drop point, penetration and mechanical stability). The samples were prepared in ratio 90:10, 50:50 and 10:90. However samples were tested for drop point by IP-396 instead of ASTM D 566 and high temperature storage stability test could not be conducted. Compatibility data of conventional polyurea grease produced as per old composition with lithium complex and calcium sulfonate grease are tabulated in table-5. The grease was first tested for drop point and drop point data indicate that drop point of mixture both (50: 50 and 10:90 mixtures) is less than either of the grease alone and similar trend is in case of penetration and thus this polyurea grease is incompatible with both lithium complex and calcium sulfonate grease. However more detailed study is needed to comprehend this observation but due to non-availability of old samples this could not be pursued further. On the other hand, compatibility data of improved grease with lithium complex and calcium sulfonate grease are tabulated in table-6. The drop point data as presented in table indicate that the drop point of the mixed greases falls within the drop point of two individual greases or within the repeatability limits of test. Interestingly penetration and mechanical stability data also falls within the limits of the two individual greases and indicating improved or at least borderline compatibility of this improved polyurea grease with lithium complex and calcium sulfonate grease. However, more studies have been planned on more samples to establish this observation.

Conclusions:

The polyurea greases are integral part of grease lubrication technology and exhibit certain unique characteristics which probably cannot be supplemented by other greases. The volume and awareness to use these greases is growing in the industry and subsequently their market share is likely to grow in future. The efforts made in authors' laboratory were to improve polyurea grease technology so as to make it more users friendly and also to make it conveniently safe manufacture in plant. The polyurea greases made by us initially demonstrated limitations like storage hardening and limited shelf life. The improved grease developed has exhibited good mechanical stability, unusually outstanding extreme pressure properties, and good water resistant and anti-rust properties. Additionally , preliminary studies conducted on this grease has indicated its comparatively improved compatibility with lithium complex and calcium sulfonate greases , however more studies are required to establish this interesting observation .

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Table – 1

Test Data of Conventional Polyurea Greases

S. #	Property	Method	Grease A	Grease B
1.	NLGI grade	ASTM D 217	2	1.5
2.	Thickener type	-	Polyurea	Polyurea
3.	Color	Visual	Green	Blue
4.	Base Oil viscosity	ASTM D445		
	cSt @ 40 ^{0} C		145	145
	cSt @ 100 ^{0} C		14.5	14.5
5.	Drop Point, °C	IP 396	259	257
6.	Worked Penetration, 25°C	ASTM D 217	286	305
7.	Change after 10,000 strokes		51	54
8.	Four Ball Weld load , kg	ASTM D 2596	400	400
9.	Timken OK Load , lbs	ASTM D 2509	50	50

Table – 2

Shelf Life Grease Data

Grease Details	W / Pen (Filling)	As on Nov 09			
		Unworked Pen	Worked Pen	After 10,000 Strokes	Drop Point , ^{0} C
Grease C ; # 36649 ; 04/11/07	286	229	305	361	258
Grease D; # 37726 ; 10/15/07	276	230	303	354	257
Grease E ; 38051 ; 02/14/07	282	195	292	344	254
Grease F; 38052 ; 02/15/07	279	227	301	363	261
Grease G; 39144, 05/15/07	297	235	305	364	254

Table – 3

Test data Improved Polyurea Greases

S. #	Property	Method	Grease A	Grease H	Grease I
1.	NLGI grade	ASTM D 217	2	2	1.5
2.	Thickener type	-	Polyurea	Polyurea	Polyurea
3.	Base Oil viscosity	ASTM D 445			
	cSt @ 40 ^{0} C		145	205	205
	cSt @ 100 ^{0} C		14.5	16.5	16.5
4.	Drop Point, °C	IP 396	259	277	275
5.	Worked Penetration, 25°C	ASTM D 217	288	295	303
6.	10,000 strokes		51	26	28
7.	100,000 strokes		-	30	32
8.	Roll Stability , % change	ASTM D 1831	14.5	6.4	8.4
9.	Four Ball Weld load , kg	ASTM D 2596	400	620	620
10.	Timken OK Load , lbs	ASTM D 2509	50	60	60
11.	Water Washout	ASTM D 1264		5.0 max	-
12.	Copper corrosion	IP 112		Pass	Pass
13.	Rust preventive properties	ASTM D 1743		Pass	Pass

Table – 4

Polyurea Grease in Synthetic Oil and high Viscosity Base Oil

S. #	Property	Method	Grease J	Grease K	Grease L
1.	NLGI grade	ASTM D 217	2	1	2
2.	Thickener type	-	Polyurea	Polyurea	Polyurea
3.	Color	Visual	Green	Blue	-
4.	Base Oil viscosity	ASTM D445			
	cSt @ 40 ^{0} C		456	224	100
5.	Drop Point, °C	IP 396	268	270	275

6.	Worked Penetration, 25°C	ASTM D 217	288	328	265
7.	10,000 strokes		32	28	45
8.	Four Ball Weld load , kg	ASTM D 2596	620	620	-
9.	Timken OK Load , lbs	ASTM D 2509	60	-	-

Table – 5

Compatibility study of Conventional Polyurea Grease

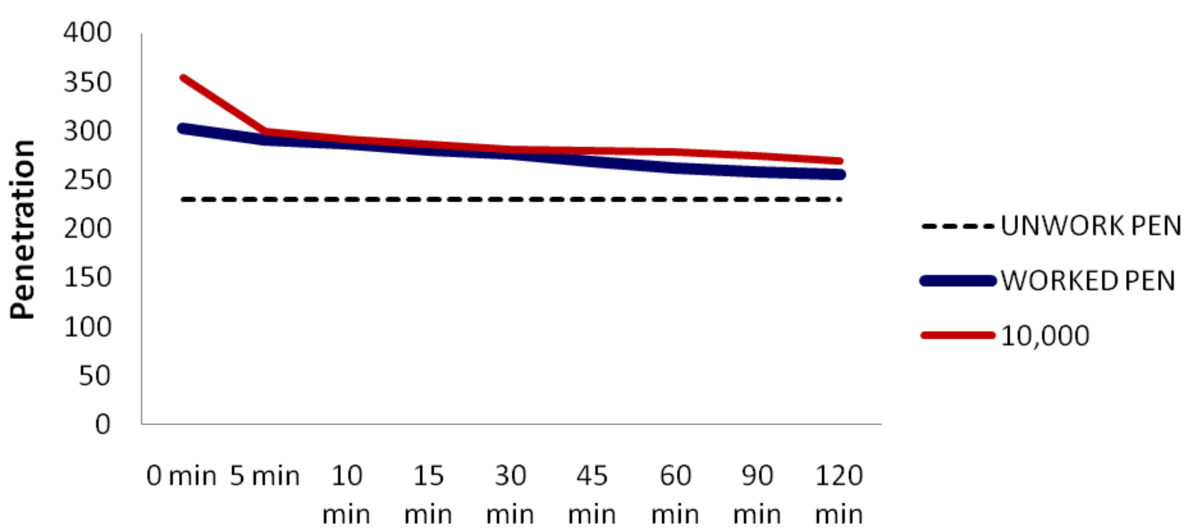
Compatibility with Li-Complex Grease				
		Drop Point , ^{0} C	Worked Pen	Weld Load
Conventional Polyurea Grease	Li- complex			
100	0	261	301	400
90	10	228	-	-
50	50	216	324	315
10	90	252	302	-
0	100	263	268	315
Compatibility with Ca-Sulfonate Grease				
Polyurea	Ca- Sulfonate			
100	0	261	301	400
90	10	-	-	-
50	50	252	310	400
10	90	272	302	-
0	100	316	280	500

Table – 6

Compatibility study of Improved Polyurea Grease

Compatibility with Li-Complex Grease					
		Drop Point , ^{0} C	Worked Pen	10,000	Weld Load
Poly Urea	Li- complex				
100	0	277	294	323	620
90	10	267	288	310	500
50	50	260	287	315	500
10	90	261	274	312	-
0	100	263	268	290	315
Compatibility with Ca-Sulfonate Grease					
Poly Urea	Ca- Sulfonate				
100	0	277	294	323	620
90	10	275	292	318	620
50	50	273	288	317	500
10	90	283	278	305	-
0	100	316	280	288	500

FIG – 1 ; Polyurea ; *Ref: 37726, 10-15-07*



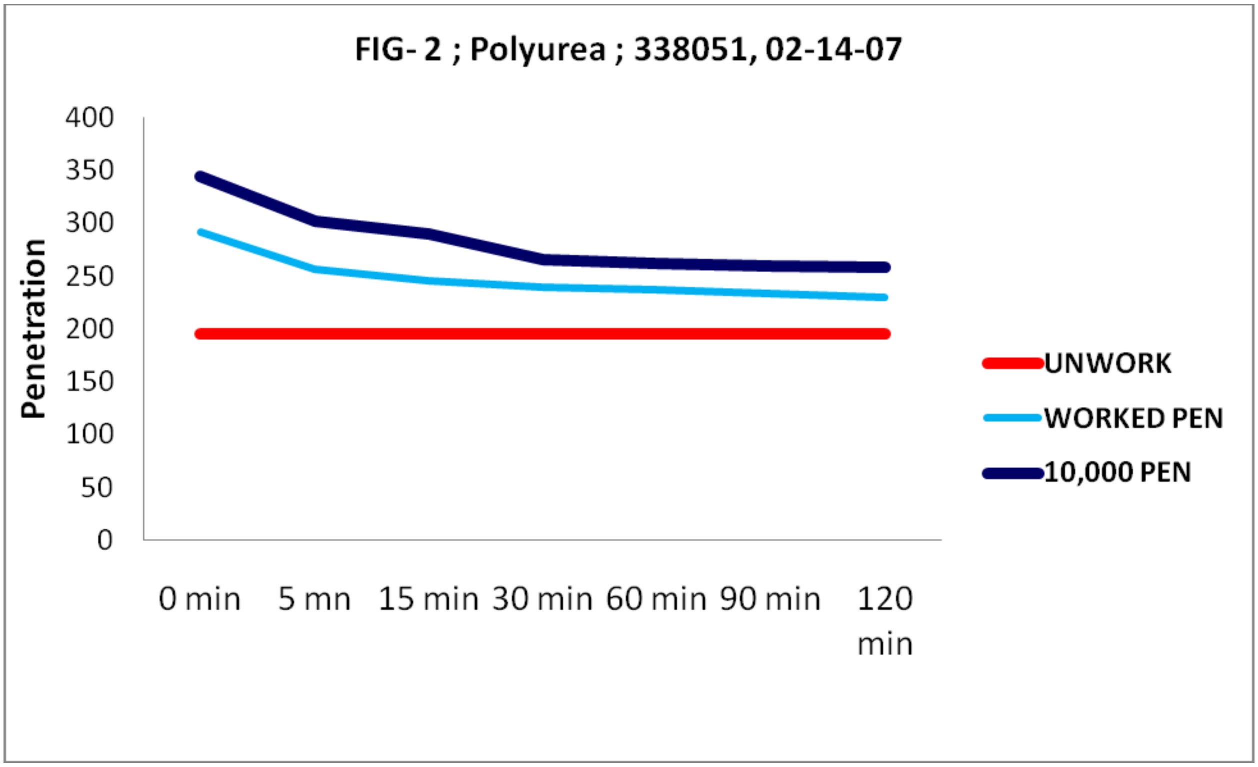


FIG- 2 ; Polyurea ; 338051, 02-14-07
Penetration
400
350
300
250
200
150
100
50
0
0 min
5 mn
15 min
30 min
60 min
90 min
120 min
UNWORK
WORKED PEN
10,000 PEN

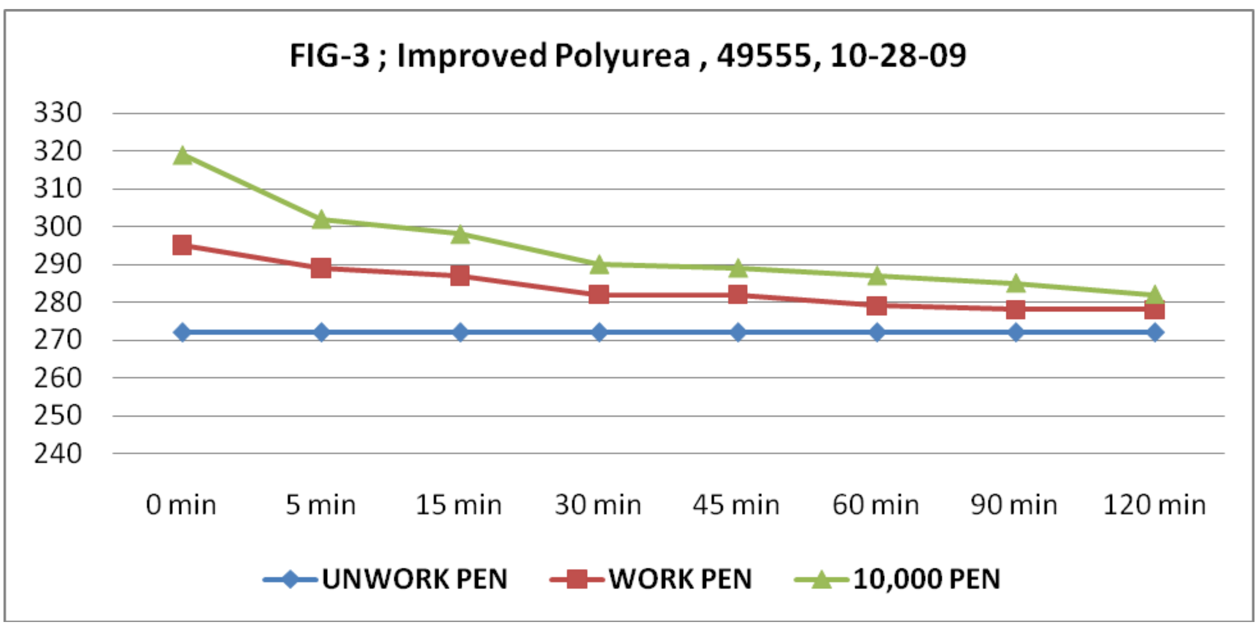


FIG-3 ; Improved Polyurea , 49555, 10-28-09
330
320
310
300
290
280
270
260
250
240
0 min
5 min
15 min
30 min
45 min
60 min
90 min
120 min
UNWORK PEN
WORK PEN
10,000 PEN

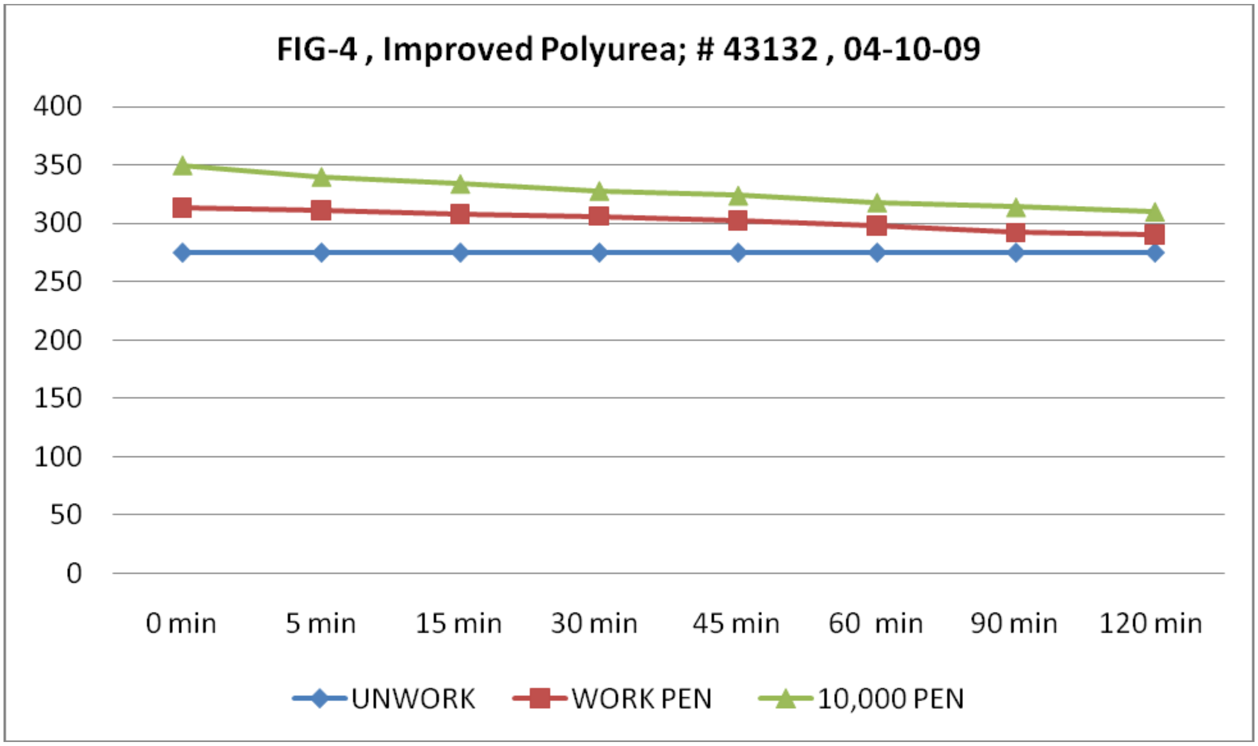


FIG-4 , Improved Polyurea; # 43132 , 04-10-09
400
350
300
250
200
150
100
50
0
0 min
5 min
15 min
30 min
45 min
60 min
90 min
120 min
UNWORK
WORK PEN
10,000 PEN