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LIGHTWEIGHT OUTSOLES FOR COMBAT FOOTWEAR

E. J. Kopka

Uniroyal, Incorporated

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A compound formulation having good abrasion resistance and flex crack resistance was developed for a combat boot outsole. The lightweight polyurethane has a specific gravity of 0.35.

To fabricate the outsole, liquid injection molding equipment was used.

In an attempt to improve flex cracking resistance a modified chevron outsole was designed.

To facilitate quality control, a Polyair flex tester was evaluated.

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TECHNICAL REPORT

74-5-CE

LIGHTWEIGHT OUTSOLES FOR COMBAT FOOTWEAR

By

E.J. Kopka
UNIROYAL, INC.
MIDDLEBURY, CONNECTICUT

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U. S. ARMY NATICK LABORATORIES
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FOREWORD

Combat footwear generally weighs 28 ounces per boot (size 9R), with at least fifty percent of this weight concentrated in the heel and sole. The minimum and maximum specific gravity of all types of solid outsoles currently being used on military footwear is between 1.1 and 1.3. The reduction of the specific gravity of outsoles to between 0.5 and 0.6 using polyurethanes is considered to be both practical and feasible, using current technology, and should result in a reduction in weight per outsole of at least 6 to 8 ounces. Based upon existing data, it is estimated that an 0.6 specific gravity expanded polyurethane outsole may possess wear capability superior to that of the solid rubber outsoles being used, and will provide at least an estimated 50% reduction in the weight of the outsole. It has been established that the excellent abrasion resistance of the solid polyurethanes can be reflected in the performance of their cellular products.

This report describes the work performed during the 20 month period from 24 June 1971, to 17 February 1973. Under the supervision of Project Officer Joseph E. Assaf, U.S. Army Natick Laboratories, the materials and processing studies and the development of fabrication procedures culminating in the fabrication of fifty pair of combat footwear with an expanded polyurethane outsole were performed by Uniroyal Inc., Middlebury, Connecticut under Project Reference 1J662713DJ40 through contract no. DAAG17-71-C-0152.

The Project Officer wishes to acknowledge Dr. Malcolm C. Henry, Deputy Director of the Clothing and Personal Life Support Equipment Laboratory (C&PLSEL), for his valued suggestions and the aid and guidance of Mr. Angus F. Wilson, Head, Rubber Technology Group at NLABS, relative to physical property requirements.

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ABSTRACT

A compound formulation having good abrasion resistance and flex crack resistance was developed for a combat boot outsole. The lightweight polyurethane has a specific gravity of 0.55.

To fabricate the outsole, liquid injection molding equipment was used.

In an attempt to improve flex cracking resistance a modified chevron outsole was designed.

To facilitate quality control, a Polyair flex tester was evaluated.

INTRODUCTION

The work described in this report was performed by Uniroyal, Inc. The goal of the work was to develop a 0.5 specific gravity closed-cell footwear outsole from liquid polyurethane polymer systems, while retaining other required physical properties such as abrasion resistance and flex crack resistance. It was desirable that the developed outsole be capable of being directly molded onto combat boot uppers.

To achieve a significant reduction in weight of the combat boot outsole, it was necessary to make full use of recent advances made in polyurethane foam technology.

The program was divided into two phases: the first phase involved the compounding and processing studies of polyurethane foam systems and the fabrication of four pair of prototypes. During the first phase, twenty additional pair of leather combat boots were fabricated for wear test by Natick Laboratories, under Contract Modification No. DAAG17-71-C-0152-P00003. The second phase was the fabrication of 50 pair of lightweight leather combat boots.

Initial compound and processing studies during phase one involved the use of casting prepolymer type compounds with a Mateer metering/mixing machine. Because the outsoles made with this method had poor flex-crack resistance, studies were undertaken to evaluate injection molded quasi-prepolymer type compounds on a Polyair liquid-injection-molding machine.

Of significant note were the development of a new outsole design, the development of a means of eliminating flex cracking of the outsole, the use of a Polyair flex tester as a means of quality control, and the fabrication of an abrasion-resistant, lightweight polyurethane sole.

I. COMPOUNDING AND PROCESSING STUDIES

A. Methods of Making Polyurethane Foam

The reactive ingredients of a polyurethane foam system usually include an isocyanate, a hydroxyl-terminated resin, and a cross-linking agent. In addition, flexible foam systems include an expanding agent as a source of gas for blowing. Three foaming methods can be employed to make flexible foam. The methods are (1) the "one-shot" method, (2) the prepolymer method, and (3) the quasi-prepolymer method. In the one-shot method, all the components (polyol, isocyanate, surfactant, expanding agent and catalyst) are combined at one time to form a foam, and the reaction is completed in "one-shot"

The prepolymer method involves the reaction of the hydroxyl compound (polyol) with an excess of isocyanate to form an isocyanate-terminated prepolymer. The prepolymer can then be mixed with the cross-linking agent, surfactant, expanding agent, and catalyst to make a "two-shot" foam. One disadvantage to the prepolymer method is the necessity for accurate metering since the weight ratio of the prepolymer stream to the curative stream can be as low as 100 to 10. Inaccurate metering would create inconsistent and poor quality foam.

The quasi-prepolymer method is a combination of the prepolymer and the one-shot techniques. Some of the polyol component is prereacted with excess isocyanate to form one of the components. Cross-linking agent, surfactant, expanding agent, and catalyst are mixed with additional polyol to form the second component. The two components are mixed, usually in equal quantities to make reproducible, good quality foam.

Only the prepolymer method and the quasi-prepolymer method were used to develop the proper outsole foam material and to fabricate the polyurethane outsoles.

B. Cast-molded Prepolymer Systems

To prepare a castable polyurethane polymer expanded with methylene chloride, a Vibrathane B-602 prepolymer based compound was used initially. The compound is listed in Table I as formulation #1. Satisfactory unit outsoles were made with this formulation, but attempts to make direct molded outsoles or test slabs resulted in foam collapse. The primary reason for the foam collapse was the condensation of methylene chloride before compound gelation and modulus buildup. To alleviate the problem of foam collapse, an improved compound was sought having the following characteristics:

1. A higher reaction exotherm for more extensive vaporization of methylene chloride.

2. Faster gel time and quicker modulus buildup after gelation.

3. Higher modulus elastomers to better withstand the differential pressure on the cell walls after methylene chloride condensation.

The first attempt at making an improved compound was to use a system based on Vibrathane B-600 prepolymer, a system demonstrably superior in the above mentioned areas. The compound can be found in Table I as formulation #2. Several unit outsoles, panels, and a pair of combat boots were made successfully without any processing problems. On flexing the foamed compound, however, a slight flex crack developed at 15,000 cycles. The flex failure is presumably due to the low molecular weight polytetramethylene ether glycol spine in the compound.

In order to retain most of the good characteristics of Vibrathane B-602, especially flex crack resistance, a slight addition of toluene diisocyanate was thought to be sufficient for higher reaction exotherm and increased modulus. The compound, as listed in Table I as formulation #3, was tried but results were inconclusive. Machine temperature settings were apparently too high causing overblowing of the compound. Freeblown samples were overexpanding followed by foam collapse. No attempts were made to make test slabs or unit outsoles.

As another attempt to increase reaction exotherm, a prepolymer which exhibits a high reaction exotherm was blended with Vibrathane B-602. In the first trial Vibrathane B-605 was blended with Vibrathane B-602. The formulation, as listed in Table I as formulation #4, processed well with rapid expansion and a short gel time. The mixture of these prepolymers, however, resulted in a composition with very low modulus causing the freeblown samples to collapse. For this reason, no test slabs or unit outsoles were made with this formulation. In the second blending trial, a formulation of Vibrathane B-602 and Vibrathane B-600 was tried (see formulation #5 in Table I). The compound processed well with proper expansion and gel time. Test slabs, unit outsoles, and two pair of boots were made with formulation #5. Physical test data for this formulation can be found in Table I. Four outsoles were flexed on the Uniroyal outsole flex tester. The first two outsoles showed no sign of flex cracking until 350,000 cycles and 870,000 cycles respectively. However, two outsoles made a week later of the same formulation showed signs of flex cracking after [illegible]0,000 cycles and 60,000 cycles respectively. (The standard for a quality outsole is 200,000 cycles without any flex cracks.) The cause for the inconsistent flex cracking data was believed to be the inconsistent mixing and metering of the compound by the [illegible] machine.

TABLE I

FORMULATIONS AND PHYSICAL DATA

(Mateer Machine)

Ingredients	#1	#2	#3	#4	#5
Vibrathane B-602	100	-	100	75	75
Vibrathane B-605	-	-	-	25	-
Vibrathane B-600	-	100	-	-	25
Toluene Diisocyanate	-	-	0.6	-	-
Methylene Chloride	10	10	10	10	10
MDA	4.1	5.0	4.0	4.1	4.0
SF1079 Surfactant	1.0	2.0	1.9	1.0	2.0
Santicizer S-160	4.1	2.8	3.6	4.1	3.8
3041 Black	2.0	2.0	2.0	2.0	2.0

Physical Test	#1	#2	#3	#4	#5	
1. Uniroyal Flex Tester	420,000 cycles	15,000 cycles	-	-	350,000 cycles (sole 1) 870,000 cycles (sole 2) 10,000 cycles (sole 3) 60,000 cycles (sole 4)	
2. Ross Flex (KC to Cut Growth)	-	-	-	-	RT	After 70 hrs. @212°F
					100% 2.3	3.5
					200% 3.8	5.5
					300% 4.8	7.5
					400% 5.8	9.0
					500% 7.0	10.5
3. Compression Deflection 25% (PSI) @ RT	-	-	-	-	120	
after steam autoclave	-	-	-	-	30	
4. Compression set % (24 hrs. @ RT) at RT	-	-	-	-	17.5	
after steam autoclave	-	-	-	-	88.4	
5. Abrasion, NBS index at RT	-	-	-	-	32	
after 70 hrs. @ 212°F	-	-	-	-	60	
6. Specific Gravity	-	-	-	-	0.6	
7. Shore A Hardness at RT	-	-	-	-	60	
after aging 70 hrs. @ 212°	-	-	-	-	55	
at 0°F	-	-	-	-	78	

The Mateer metering/mixing machine mentioned is a laboratory-size, three-component, polyurethane casting machine. By incorporating the prepolymer method, the Mateer machine was used to evaluate the compounds for processing and to make the samples for testing. The three components which are mixed and metered by the machine are (1) prepolymer, (2) curative and (3) additives, which include expanding agent and colorant. Figure 1 illustrates the essential parts of the Mateer and diagrams the paths of the components to the mixing head.

It was noted that the outsoles and the slabs made on the Mateer had poor resistance to flex cracking. The reason for the poor flex cracking resistance can be found in (a) the chemistry, (b) the processing and/or (c) the outsole design. If the diamine (curing agent) concentrations vary beyond the 1.00 - 1.10 mole ratio range, flex life is markedly decreased. If the mixing/metering machine cannot meter or mix the proper ingredient ratios consistently, the flex life will vary from outsole to outsole. If the outsole design is such that many stress areas can be found in the outsole, the flex life of the outsole will be poor.

Initially it was thought that flex cracking would be minimized by controlling the mole ratio and the skin thickness of the outsole material. However, outsoles made on the Mateer machine, in which these were regulated, have shown poor flex cracking resistance. The problem, again, is the inconsistent metering and mixing of the Mateer machine. The problem is not aided by the fact that the prepolymer curing agent ratio of 110 parts to 10 parts is difficult to meter with the necessary precision.

The two major areas of concern at this time were (1) finding a quicker flex test for screening compounds and (2) eliminating the flex cracking of the outsole. It was felt that the major cause of poor flex cracking resistance was the use of the prepolymer system and the lack of accurate metering of ingredients. By using the quasi-prepolymer system on a Polyair liquid-injection-molding machine, the ingredient ratios would be in the range of 100/100 to 100/50 all of which helps improve the accuracy and the uniformity of mixing and metering. Formulations tried on a Polyair LIM will be discussed later.

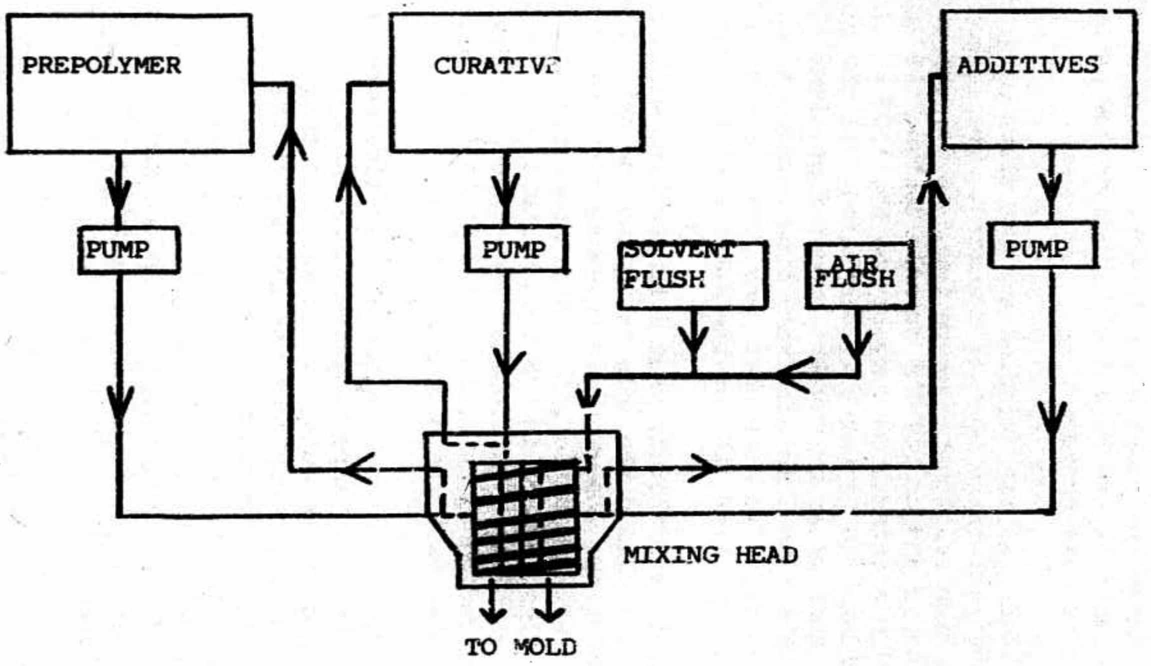


FIGURE 1 - SCHEMATIC OF MATEER METERING/MIXING MACHINE

C. Flexing

One of the most important properties of compounds for potential outsole use is flex life. Two standard tests presently exist for determining flex life of slab materials - the DeMattia flex test and the Ross flex test. Both of these tests are rather mild and are not very sensitive to compounding variables in foam systems. UniRoyal Footwear has been using a flexer of their own design for the quality control of finished shoe parts requiring a degree of flex crack resistance. This particular flexer was also used in this work to determine the optimum formulation for outsole compounds to be used in combat boots. A drawing of the flexer is shown in Figure 2. A sample 1" X 4" ¼" cut through the middle parallel to the flex axis is clamped in the flexer jaws. The jaws open and close at a rate of 100 times/minute. Maximum distance when open is 2 inches which is reduced to ½ inch when the jaws are closed.

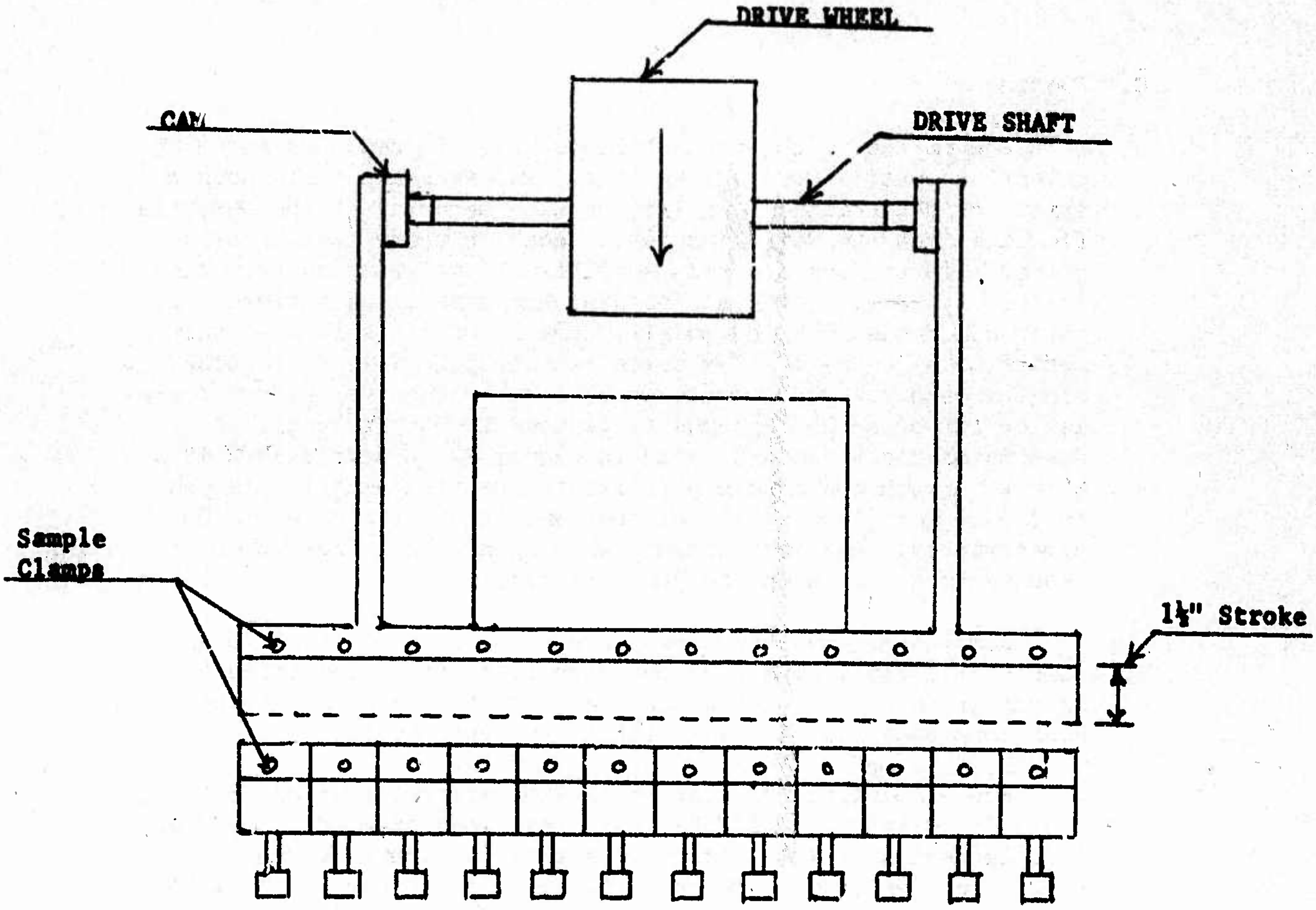
Samples are measured for percent cut growth after a designated number of cycles. The test has been found to be sensitive to a 2% variation in mole ratio and takes about five hours to complete. Poor compounds usually fail within the first hour.

For a specific formulation of 2000 molecular weight PTMG/TDI (tolylene diisocyanate)/MPDA (meta phenylene diamine), the flex life is best at a 1.05 ratio (less than 10% crack growth at (50,000 cycles); decreases slightly at a 1.08 mole ratio (150% crack growth); and decreases sharply below 1.02 mole ratio (greater than 200% crack growth @ 50,000 cycles). Figure 3 illustrates these results.

The Polyair flex tester, a quick and accurate flex test, can also be used for screening compounds. This instrument (illustrated in Figure 4) tests the resistance against further tearing of an already existing cut when subjected to impact at the moment of maximum bending strain. The outsole slab sample to be tested is 25 mm X 250 mm X 6 mm and is held in place between two clamps which bend the material 110°. At the moment of maximum bending strain, the sample is thrown against a pivoted hammer. The material must undergo impact bending stress 6,000 times per hour. The material is tested for 100% (5 mm) tear propagation. If less than 5,000 bends produce a growth of more than 100%, the material must be further tested for total break (25 mm).

If the number of bends leading to total break is less than 15,000 the tested material has failed the test. The total time for the test is less than three hours. This flex test has been used to evaluate all formulations tried on the Polyair LIM and the best prepolymer type formulations tried on the Mateer.

Scale = Approximately 1/4



Speed: 100 Cycles/Min.
Stroke: 1½ In.

Clearance at Closed Position = 2 X Sample Thickness

Sample Size: 1" X 4" X 1/4"

A 1/4" cut extending through the sample is made in center of sample parallel to flex axis prior to flexing.

Figure 2 - UniRoyal Reciprocating Flexer - Top View

Results of PTMG/TDI/mPDA Formulations evaluated with
UniRoyal Flex Tester

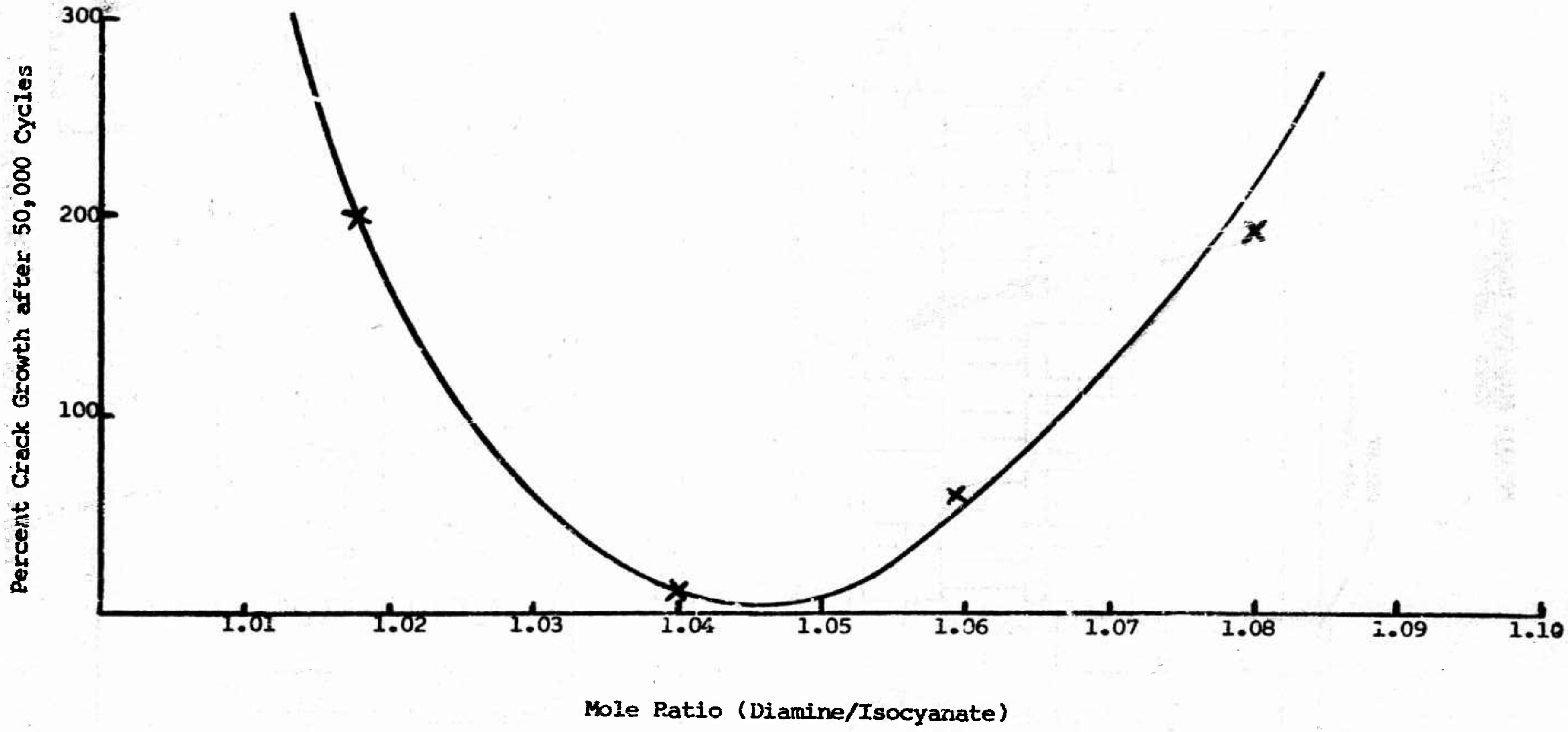


Figure 3 - Percent Crack Growth vs. Mole Ratio

POLYAIR FLEX TEST MACHINE - FIGURE 4
SCALE - APPROX. ¼" = 1"

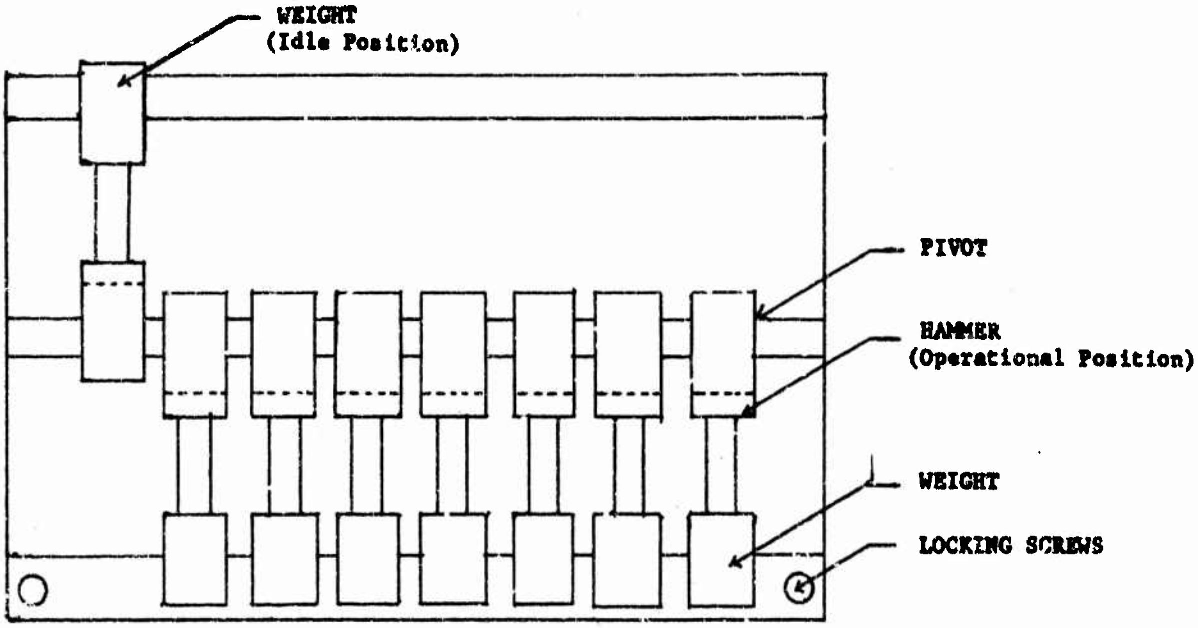


FIG. 4A - TOP VIEW - HAMMERS AND WEIGHTS

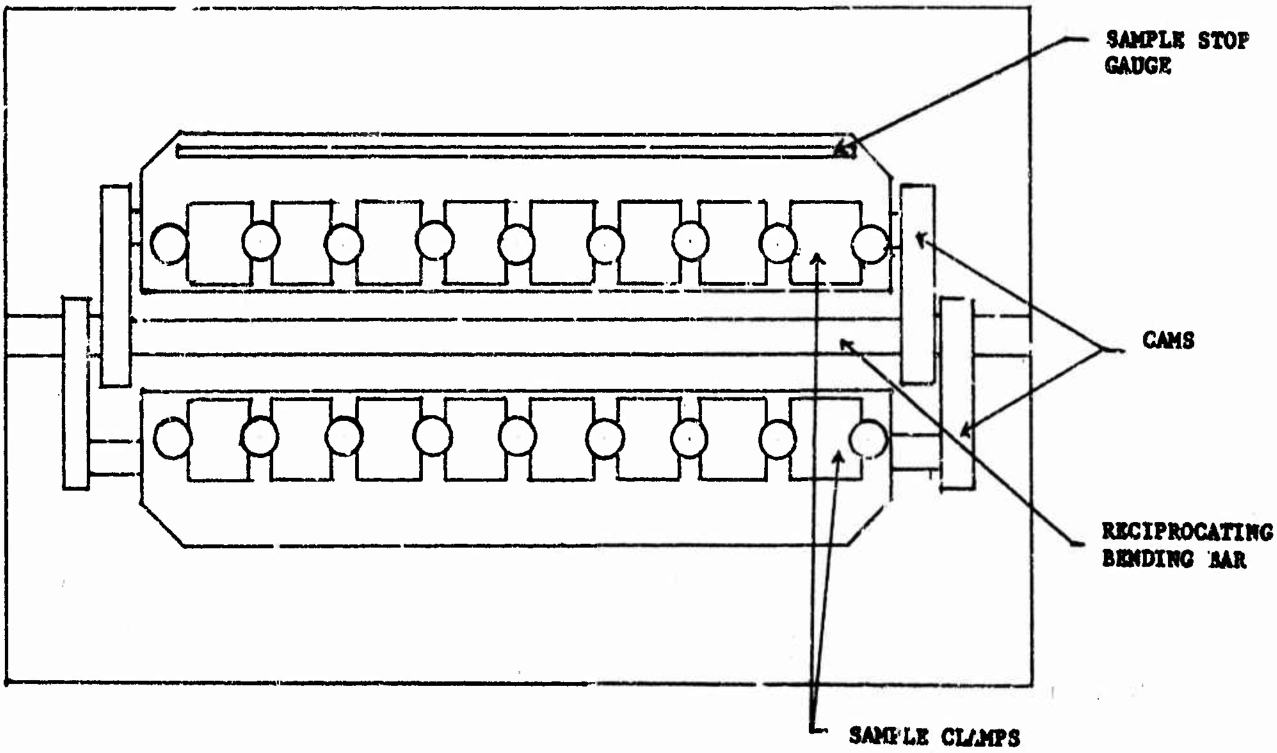


FIG. 4B - TOP VIEW - SAMPLE HOLDER AND FLEXER

POLYAIR FLEX TEST MACHINE - FIGURE 4
SCALE ½" = 1"

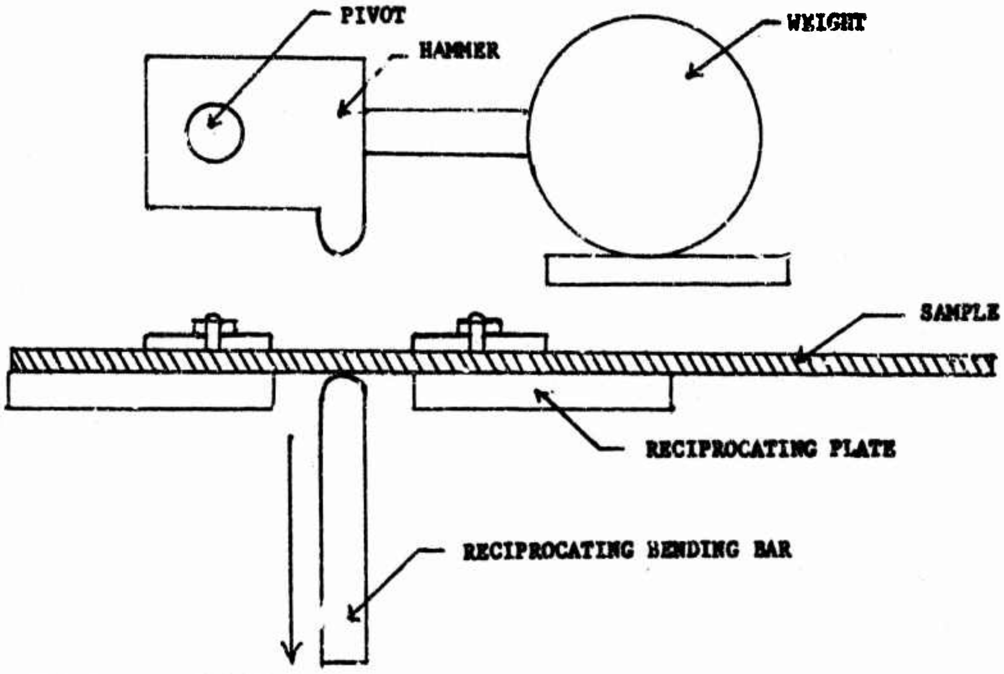


FIG. 4C SIDE VIEW - DOWN STROKE

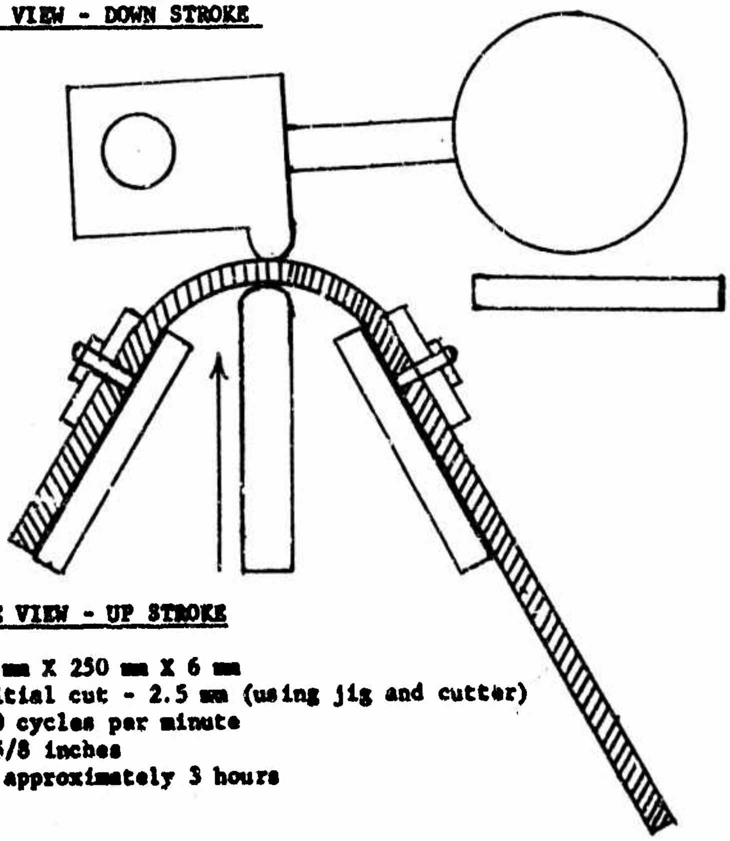


FIG. 4D SIDE VIEW - UP STROKE

Sample - 25 mm X 250 mm X 6 mm
Initial cut - 2.5 mm (using jig and cutter)
Speed - 100 cycles per minute
Stroke - 1 5/8 inches
Test time - approximately 3 hours

D. Skin Thickness

During initial screening of prepolymer type compounds for combat boot outsoles, it was observed that the abrasion resistance of expanded polyurethane compounds can be substantially increased by forming a high density layer (skin) at the outsole wear surface. With chemically expanded formulations, this can be readily accomplished by control of the mold temperature. Figure 5 is a plot of skin thickness versus mold temperature for a 0.4 specific gravity PTMG/TDI/mPDA/Nitrosan-blown system. Skin thickness from 0 to 1/8 inch can be readily obtained by varying the mold temperature from 230° to 100°F. Similar relationships exists for other chemical blowing systems. The temperature for no skin formation is usually the boiling point of the solvent blowing agent (i.e. 180°F for methylene chloride) or the decomposition temperature of the chemical blowing agent (i.e. 230°F for Nitrosan).

Several outsoles were cast in a mold having a sharp-cleat outsole design (Panama outsole). Even though the formulation was optimized according to the flex-test results of core samples (samples having the outer skin removed leaving uniform density material) early failure (at 10,000 cycles) was encountered at the cleat-base area on a UniRoyal outsole flexer. This machine flexes an outsole 90° at the rate of about 50 cycles per minute. No outsole cracking in 200,000 cycles is considered standard for UniRoyal commercial products.

A study was made to determine the relationship of skin thickness to crack resistance. The results are shown in Figure 6. As can be seen, good flexing can be obtained with high skin thickness outsoles or uniform density (no skin) outsoles. The moderate skin thickness outsoles are the most susceptible to flex cracking. These results can be explained by observing the cross section of skin formation around sharp corners.

Figure 7 shows three skin thicknesses for a Panama outsole design. The moderate skin thickness is well defined in cleat areas but tends to thin out around sharp corners. During flexing action, most of the bending stress is concentrated in this reduced hardness, lower modulus area resulting in early failures. With heavy skin or no skin outsoles, the surface integrity is maintained and no severe stress areas are developed.

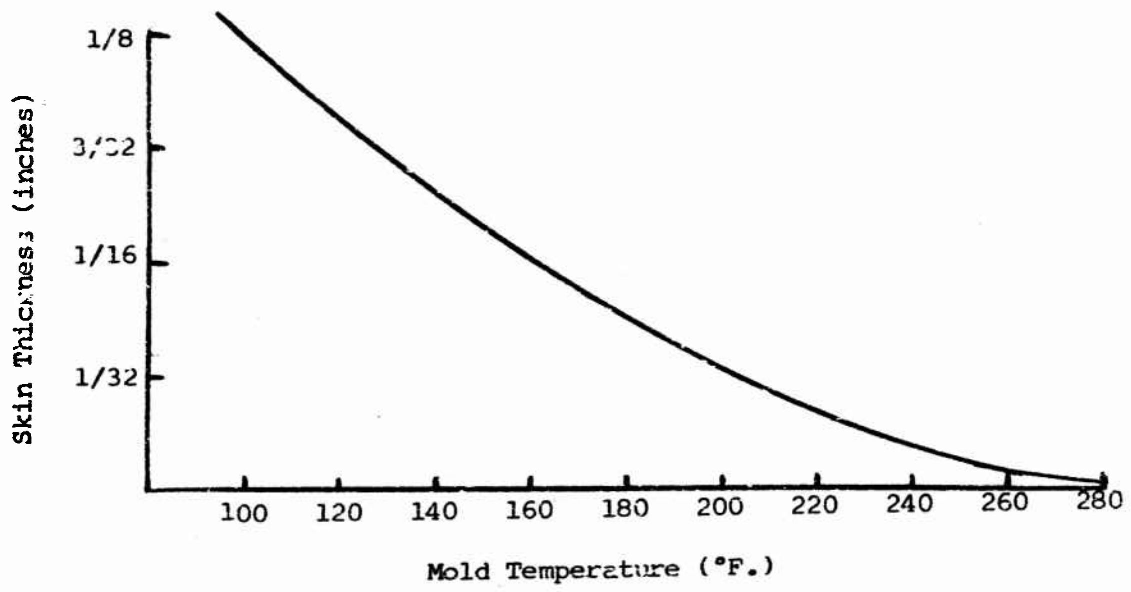


Figure 5 - Outsole Skin Thickness vs. Mold Temperature (Nitrosan Blown Formulations)

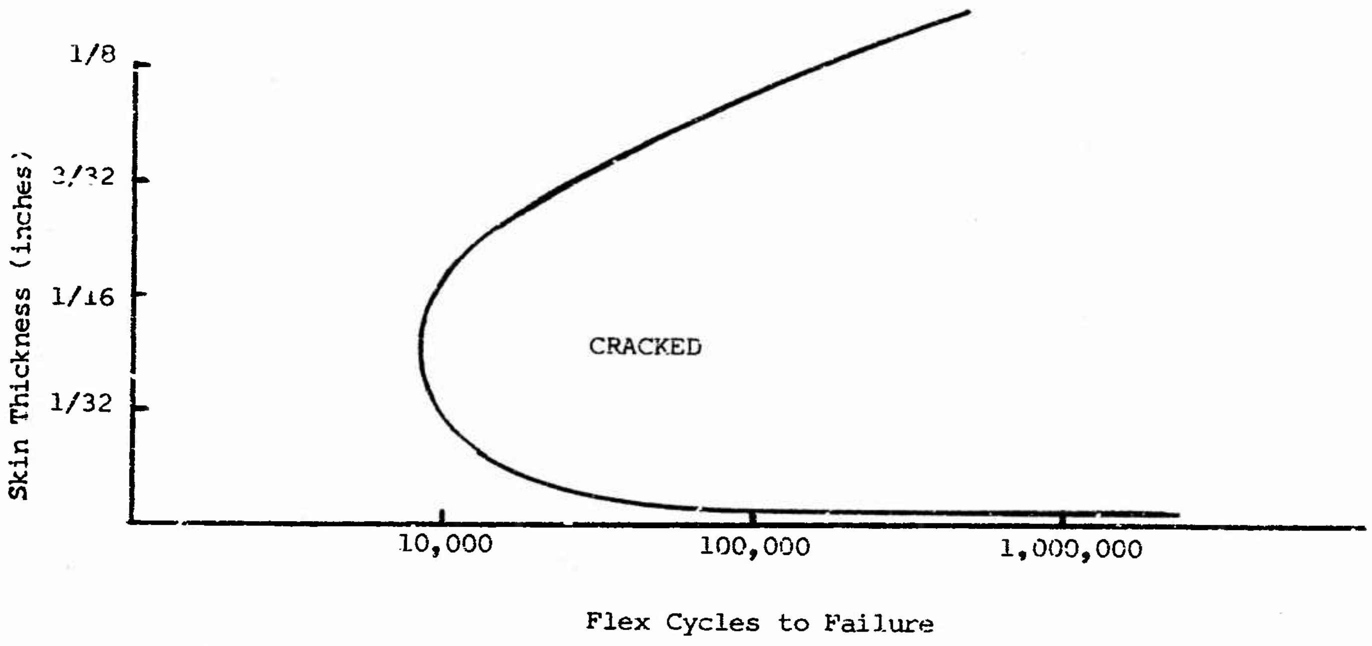
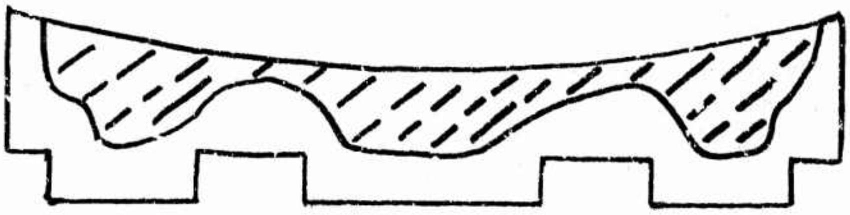
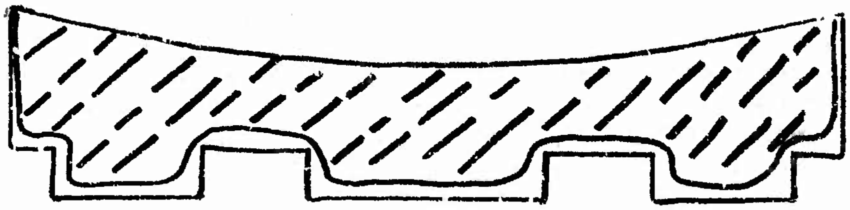


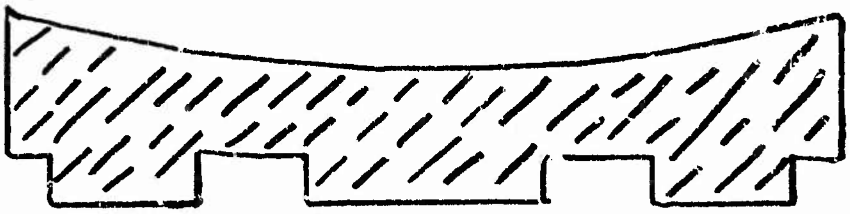
Figure 6 – Skin Thickness vs. Outsole Flex Life (Nitrosan Blown Formulations)



Heavy Skin



Medium Skin



No Skin

Figure 7

Integral Skin Formation in Deep Cleat Areas of Outsoles

E. Injected Quasi-prepolymer systems

The second approach to the compound studies involved the use of the quasi-prepolymer method in making the outsole. A Polyair liquid-injection-molding machine was used to evaluate compounds for processing and to make samples for testing. The Polyair LIM is a six-station, three-component, polyurethane injection machine. As illustrated in Figure 3, the three components which are mixed and metered by the machine are (1) quasi-prepolymer, (2) curative (polyol and crosslinking agent) and (3) pigment. The weight ratio of the mixture is held constant since the drive of the component pumps are synchronized via chain gears to maintain the ratio of the mixture. With the weight ratio being constant, the necessity of a pre-shot of off-ratio compound prior to injection is eliminated. The components are mixed in a mixing head, whose screw is driven at 18,000 RPM, which provides better mixing than the Mateer mixing head. The compounds evaluated were basically (1) polyester/MDI quasi-prepolymers cured with polyester polyol/1,4 butanediol and (2) polyether/MDI quasi-prepolymers cured with polyether polyol/1,4 butanediol. All compounds evaluated were expanded with water incorporated in the curative.

Formulations using the prepolymer method and tried on the Mateer machine were discussed in Section I,B. For reference, two compounds made on the Mateer, formulations No. 1 and No. 2, have been included in Table II. The methylene chloride blown compound (#1) had good abrasion resistance (NBS index - 95), but the outsole had a poor flex life, when tested on the UniRoyal flexer. The Nitrosan blown compound (#2) had less abrasion resistance (NBS index - 40), but had excellent flex life.

The remaining formulations in Table II (No. 3 - No. 12) incorporated the quasi-prepolymer method and were expanded with water. These formulations were all made on the Polyair LIM. A polyester polyol from Mobay Chemical was used in formulations. No. 3 and No. 4; MDI (isocyanate) and 1,4 butanediol were used in all formulations on the LIM. The first trial with the Mobay polyester polyol (formulation No. 3) failed when the outsole material did not pass the flex test on the Polyair flex tester described earlier. The second trial (formulation No. 4) passed the flex test, but the NBS abrasion index was only 52.

No. 5 is a formulation developed by the UniRoyal Chemical Division. It is also a polyester-based, water-blown system. This formulation passed the Polyair flex test and the outsole material had an NBS abrasion index of [illegible]. No. 6 is a formulation currently being used by UniRoyal on Polyair equipment in Spain. The flex life of the outsole material is not optimum, but the abrasion resistance is excellent (NBS abrasion index - 268).

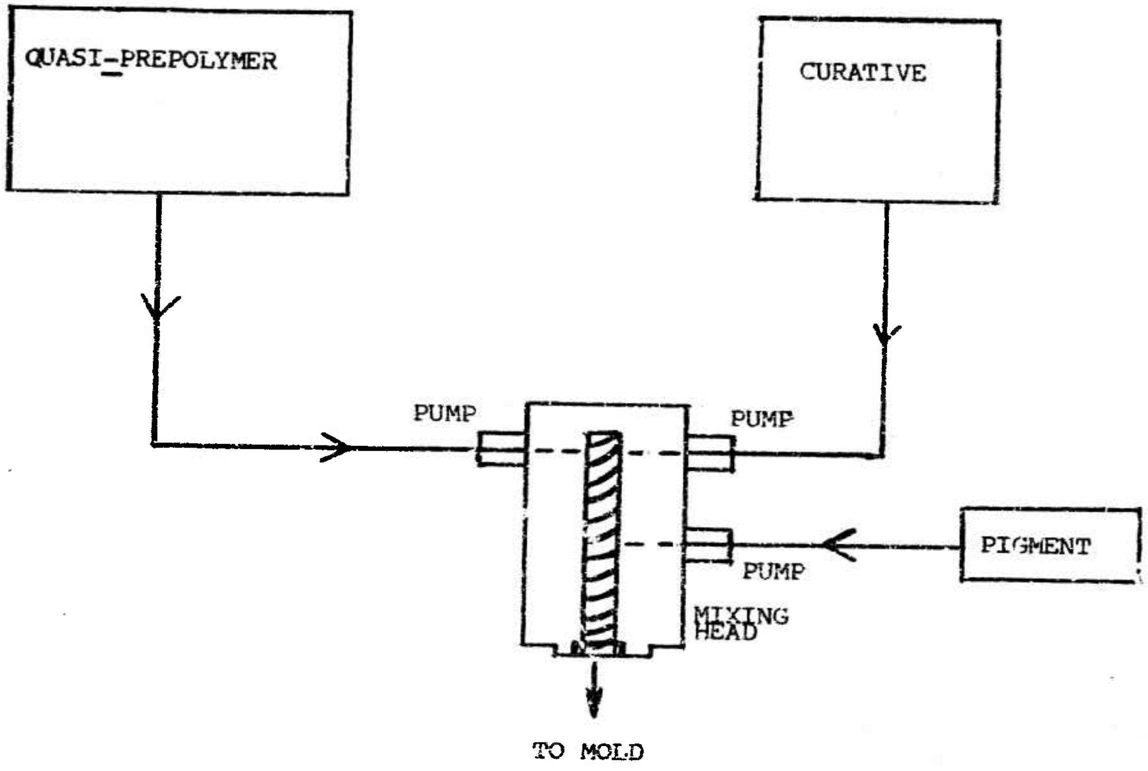


FIGURE 8 - SCHEMATIC OF POLYAIR LIM

TABLE II PHYSICAL DATA ON OUTSOLE FORMULATIONS

FORMULATION	EXPANDING AGENT	EQUIPMENT USED	DENSITY	SHORE A HARDNESS	FLEXING UNIROYAL FLEXER	FLEXING POLYAIR FLEXER 5000 bends	FLEXING POLYAIR FLEXER 15000 bends	NBS ABRASION INDEX
1. Polyether polyol/mPDA (Uniroyal)	Methylene Chloride	Mateer	32	75	65,000	--	--	95
2. Polyether polyol/mPDA (Uniroyal)	Nitrosan	Mateer	32	60	550,000+	--	--	40
3. Polyester polyol/MDI/1,4 butanediol (Mobay) - 1st trial	Water	Polyair LIM	40	65	--	OK	failed @ 7000	--
4. Polyester polyol/MDI/1,4 butanediol (Mobay) - 2nd trial	Water	Polyair LIM	40	60	--	OK	OK	52
5. Polyester polyol/MDI/1,4 butanediol (Uniroyal Chem.)	Water	Polyair LIM	41	52	--	OK	OK	81
6. Polyester Polyol/MDI/1,4 butanediol (Bayer)	Water	Polyair LIM	35	48	--	380%	failed @ 10,000	288
7. Polyether polyol/MDI/1,4 butanediol (Uniroyal) - 1st trial	Water	Polyair LIM	38	68	--	failed @ 4900	--	--
8. Polyether polyol/MDI/1,4 butanediol (Uniroyal) - 2nd trial	Water	Polyair LIM	38	75	--	300%	failed @ 7000	

TABLE II PHYSICAL DATA ON OUTSOLE FORMULATIONS (CONT'D)

FORMULATION	EXPANDING AGENT	EQUIPMENT USED	DENSITY	SHORE A HARDNESS	FLEXING			NBS ABRASION INDEX
					UNIROYAL FLEXER	POLYAIR FLEXER 5000 bends	POLYAIR FLEXER 15000 bends	
9. PPG Polyol/MDI/1,4 butandeiol (Dow Chem.)	Water	Polyair LIM	40	52	--	220%	540%	--
10. Polyester Polyol/PTMG/MDI/1,4 butanediol (Mobay)	Water	Polyair LIM	37	64	--	failed @ 3000	--	--
11. Polyester Polyol /MDI/1,4 butanediol (2000 and 2001 - Mobay)	Water	Polyair LIM	40	65	--	no growth	no growth	--
12. Polyether Polyol/HMDI/1,4 butanediol (Dupont)	Water	Hand-Cast	33	60	--	failed @ 2300	--	--

Formulations No. 3 - No. 6 represent the type of compounding that was known to process well on the Polyair LIM. Realizing that a polyester-based outsole material may have limitations if used as combat boot soling material, formulation No. 7 was an attempt to use a PTMG polyether-based compound in the LIM. Formulation No. 7 failed at 4900 bends on the Polyair flexer based on a standard of 15,000 bends. A second trial (#8) using the PTMG polyether polyol but modifying the processing, showed improved flex life, however, the compound failed at 7000 bends. A polypropylene glycol (polyether) was used in formulation No. 9. The compound processed well and passed the flex test. This compound, however, has not shown consistent results in other trials, samples of which have failed prematurely on the flexer. The cause of the inconsistent flex data is not known and the more involved studies necessary to determine the cause would have gone beyond the timetable of this contract.

Formulation No. 10 involved using polyether polyol in the quasi-prepolymer and polyester polyol in the hardener. Although it is generally accepted that a poor compound results from combining a polyether and a polyester in the same compound, #10 processed well with good cream time (20 seconds) and good cure time (5 minutes). On the flex tester, however, the compound failed at 3,000 bends. In an attempt to improve the processing of formulation #4, two polyester polyols were used (#11). The 2000 type polyester is solid at room temperature while at the same temperature the 2001 type polyester is a viscous liquid. The compound did process better than #4, and showed no signs of cut-growth at 5,000 bends or 15,000 bends on the Polyair flexer.

To use technology developed for a white lightweight insulated boot to the best advantage, #12 was formulated to incorporate PTMG and hydrogenated MDI to make an outsole with a hardness of 60 Shore A. Compound #12 was hand-cast into molds set-up on the Polyair LIM and samples failed on Polyair flexer at 2300 bends. The compound failed the flex test because hand-cast samples tend to be poorly mixed and not representative of machine-made samples. The samples were hand-cast because the LIM was not equipped to meter the 100 to 22 weight ratio needed.

Of the twelve formulations evaluated, formulations #4 and #11 were judged the best overall considering physical properties and ease of processing. Formulation #11, however, did exhibit the best flex life and #11, therefore, was used in fabrication of wear test boots.

As proof that outsole material made from formulation #11 is indeed closed-cell foam, photographs were taken of foam samples using a scanning electron microscope. Figure 9a illustrates the type of cell structure achieved using formulation #1. This methylene chloride expanded compound has a non-uniform, predominately open-cell (ruptured) structure. Figure 9b illustrates the type of cell structure achieved using formulation #11. This water-expanded (CO_2 generated) compound has a uniform, fine closed-cell structure.

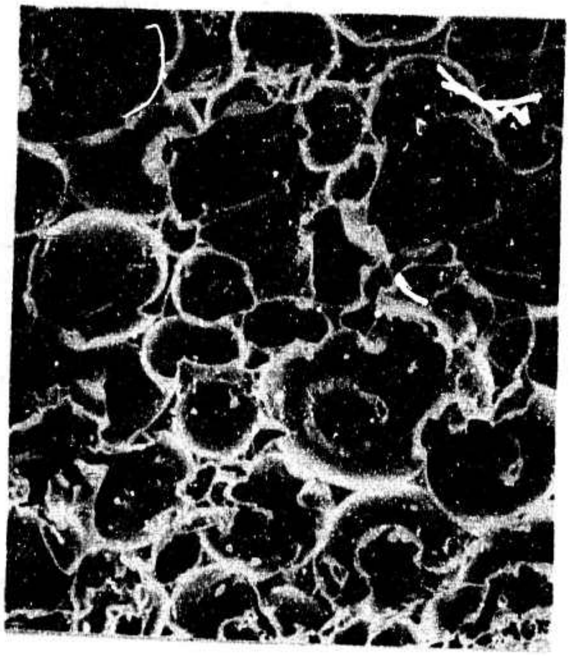


Fig. 9a - Formulation #1
METHYLENE CHLORIDE EXPANDED

(60x)

Fig. 9b - Formulation #11,
WATER EXPANDED

(60x)

Figure 9 - SCANNING ELECTRON MICROSCOPE PHOTOGRAPHS OF OUTSOLE MATERIALS

II. MOLDS

The fabrication of combat boot outsoles and test slabs on the Mateer machine was done using two metal molds furnished by U.S. Army Natick Laboratories. The molds incorporated (1) a Panama design outsole and (2) a chevron design outsole. These outsole designs are illustrated in Figures 10 and 11 respectively.

As previously mentioned, one reason for the poor flex cracking resistance of the outsole compounds can be found in the outsole design. In an attempt to eliminate the high stress areas in the outsole, the Design Center at UniRoyal's Naugatuck Footwear Plant designed a variation of the chevron outsole design. The modified design is illustrated in Figure 12.

To use the Panama type molds or the modified chevron type molds on the Polyair LIM, it was necessary to modify mold halves and lasts to fit on the Polyair turntable. To inject compound, an injection port was drilled in the toe portion of each mold.

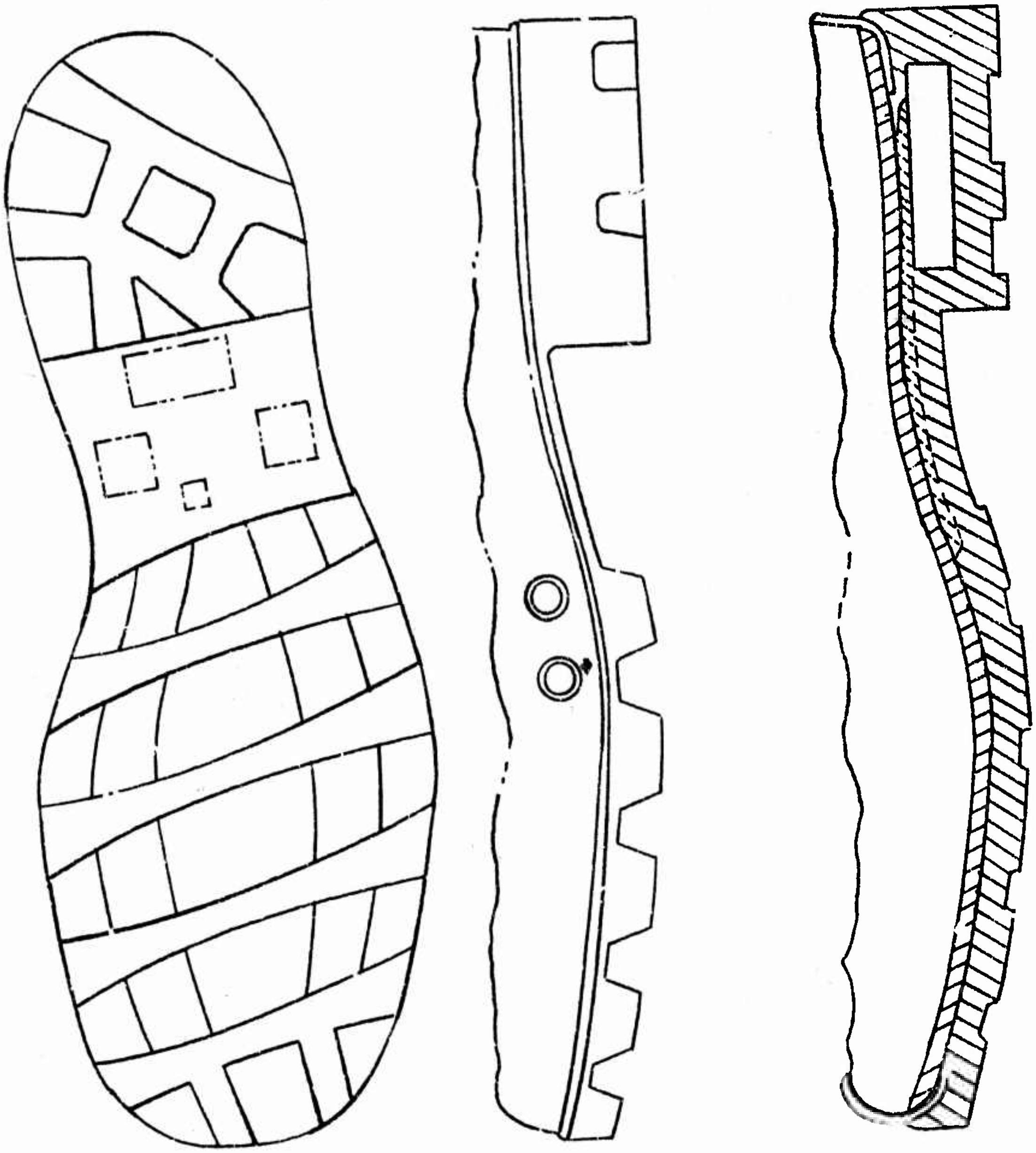


Figure 10 - Panama Design Outsole

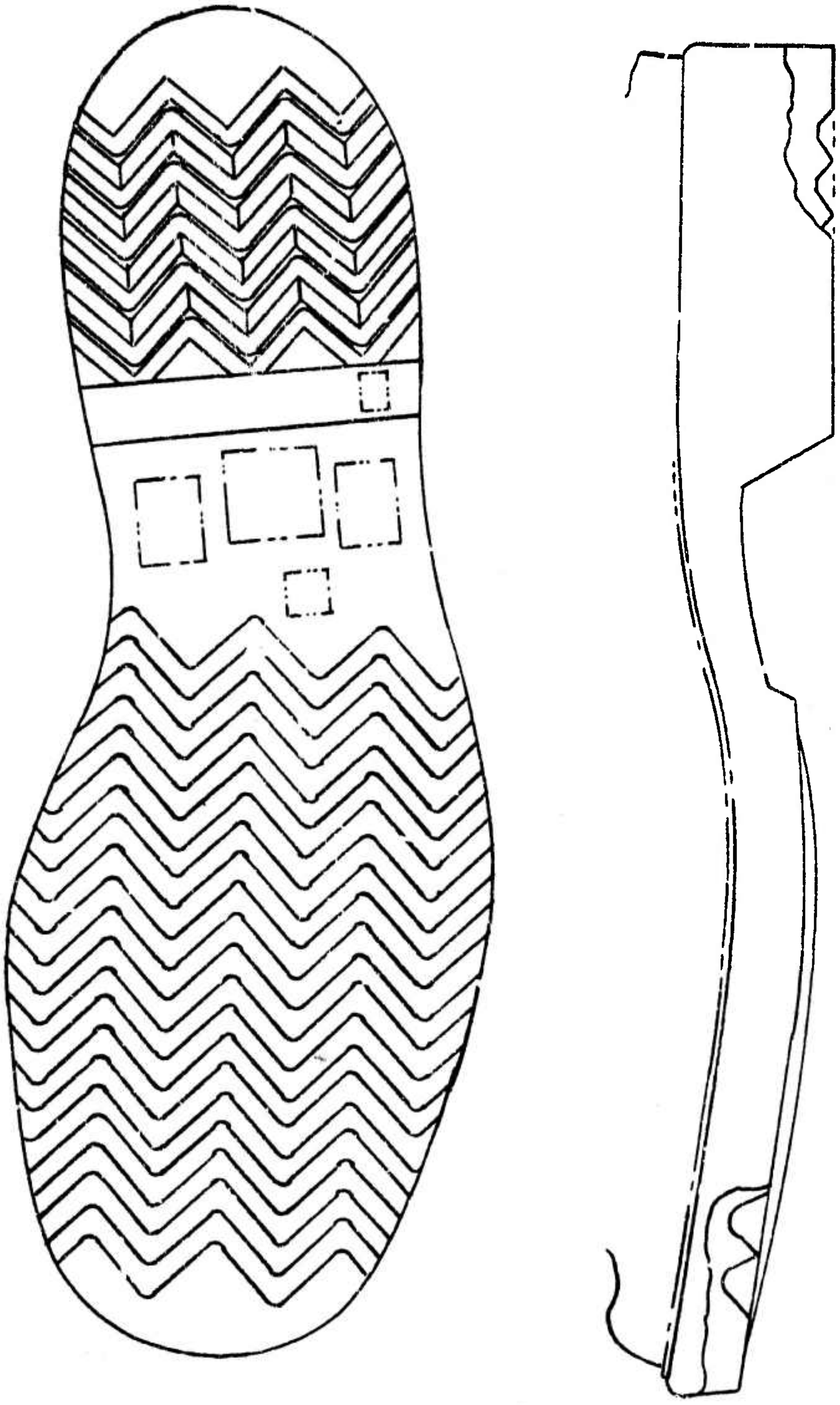


Figure 11 - Chevron Design Outsole

Figure 12 - Modofied Chevron Design Outsole

III. PROTOTYPES

Prototype pairs of boots were made at various times during the contract. The formulations used are given below. Using the prepolymer method, the Mateer metering/mixing machine was used to fabricate prototype pair #1 and prototype pair #2. Both prototypes were made by casting material into the Panama type outsole molds and placing the lasted upper onto the closed outsole mold rings. The first prototype was expanded with a halocarbon, methylene chloride, and the second prototype was expanded with a chemical blowing agent, Nitrosan. The following formulations apply to these prototypes:

	Formulation	
	#1	#2
Vibrathane B-602	100.0 parts	100.0 parts
Methylene Chloride	10.0	---
mPDA	4.1	4.0
SF1079 Silicone Surfactant	1.0	0.5
Santicizer S-160	4.1	5.5
Nitrosan	--	0.6
3041 Black	2.0	2.9
US-15N	--	0.3
Prepolymer temp.	160°F	240°F
Curative temp.	225°F	190°F
Additive temp.	RT	RT
Mold temp.	195°F	230°F
Preshot time	2 sec	2 sec
Demold time	5 min.	5 min.
Post Cure	2 hrs. at 200°F	2 hrs. at 200°F

The third prototype pair was fabricated on the Polyair LIM using the quasi-prepolymer technique. The compound was injected into the assembled Panama-type outsole mold. The following formulation which is the same as formulation #11 in Table II applies to prototype pair #3:

	Formulation
Multrathane R14	22.5 parts
Multrathane F222	77.5
MDI	40.0
1,4 butanediol	10.0
Water	0.2
Dabco catalyst	0.4
T-9 catalyst	0.1
DC193	0.3
3041 Black	2.0
Quasi-prepolymer temp.	120°F
Curative temp.	120°F
Additive temp.	RT
Mold temp.	110°F
Preshot time	none
Demold time	5 min.
Post cure	24 hrs. at RT

IV. SERVICE TESTS

A total of five pair of combat boots were fabricated for forced wear-testing. Information regarding the boots can be found in Table III. Forced wear testing of the boots was conducted by U.S. Army Natick Laboratories. The forced wear test involved construction workers in the Boston area who wore the boots on asphalt and gravel surfaces. Results indicated that pair #3 had the best wearing (flex life and abrasion resistance) compound. Forced-wear testing conducted by UniRoyal at the Naugatuck Footwear Plant substantiated those results. The UniRoyal forced wear test involved test boots being worn under controlled conditions over a prescribe route of paved and concrete walkways.

V. PAIRS FOR WEAR TESTS

A. Twenty Pair

Under Contract Modification Number DAAG17-71-C-0152-P00003, twenty pair of combat boots were fabricated using formulation #5 listed in Table I. Ten pair were made with the Panama design outsole and ten pair were made with the chevron design outsole. All twenty pair were made using the Mateer metering/mixing machine. Data pertaining to the twenty pair can be found in Table IV.

Extensive wear testing of the boots conducted by the U.S. Army Natick Laboratories indicated that many of the boots had poor flex life and abrasion resistance. As a result of this testing, use of the quasi-prepolymer method on the Polyair LIM to make the outsoles become the prime objective. The poor and inconsistent wear properties of the twenty pair were mainly caused by improper metering and mixing of the Mateer machine.

B. Fifty Pair (Phase II)

During Phase II, fifty pair of combat boots were fabricated on the Polyair LIM using the modified chevron outsole mold. As indicated in Table V, twenty-five pair were made with an outsole compound having a specific gravity of 0.70 and twenty-five pair having a specific gravity of 0.55. The compound for all the fifty pair is the same as the compound used for prototype pair #3. Test slabs, made after every second pair of boots, were used as a means of quality control during boot fabrication. The Polyair flex test was performed on the test slabs and the data generated was applicable to the two pairs of boots fabricated prior to the making of the test slab. This time period for making each group of two pairs and one test slab was approximately 25 minutes. The pairs of boots, as listed in Table V, do not represent the order of fabrication because several pairs were replaced due to incomplete filling or poor alignment of the outsoles.

TABLE III DATA ON WEAR-TEST BOOTS

		NO.	OUTSOLE DESIGN	MATERIAL	FORMULATION #	UPPER WEIGHT	OUTSOLE WEIGHT	TOTAL WEIGHT
PAIR ONE	LEFT	0110B	CHEVRON	ETHER/MDI/H_2O	8	405g.	180g.	585g.
	RIGHT	0110K	PANAMA	ETHER/ESTER/H_2O	10	408g.	216g.	624g.
PAIR TWO	LEFT	0110H	MOD. CHEV.	ETHER/ESTER/H_2O	10	411g.	230g.	641g.
	RIGHT	0110J	PANAMA	ETHER/ESTER/H_2O	10	402g.	180g.	582g.
PAIR THREE	LEFT	0110N	MOD. CHEV.	ESTER/MDI/H_2O	11	416g.	244g.	660g.
	RIGHT	0110P	PANAMA	ESTER/MDI/H_2O	11	402g.	218g.	620g.
PAIR FOUR	LEFT	0110R	CHEVRON	ESTER/MDI/H_2O	11	402g.	218g.	620g.
	RIGHT	0110Q	PANAMA	ESTER/MDI/H_2O	11	402g.	217g.	619g.
PAGE FIVE	LEFT	0110T	MOD. CHEV.	LD3056/HMDI/H_2O	12	369g.	226g.	595g.
	RIGHT	0110S	PANAMA	LD3056/HMDI/H_2O	12	377g.	221g.	598g.

TABLE IV

DATA APPLICABLE TO THE TWENTY PAIR OF COMBAT BOOTS
(MODIFICATION #DAAG 17-71-C0152-P00003)

Weights:

Heel Plug	10	grams
Shank	23.5	grams
Hot melt adhesive	4.5	grams
Lace	7	grams
Comfort inner sole	11	grams
	56	grams for all Boots

Boot #	Total Boot Weight	Upper Weight	Outsole Weight
1	577 grams	347 grams	174 grams
2	582 grams	351 grams	175 grams
3	579 grams	341 grams	182 grams
4	591 grams	354 grams	181 grams
5	606 grams	355 grams	195 grams
6	574 grams	344 grams	174 grams
7	608 grams	361 grams	191 grams
8	589 grams	356 grams	177 grams
9	591 grams	356 grams	179 grams
10	595 grams	344 grams	195 grams
11	590 grams	339 grams	195 grams
12	589 grams	342 grams	191 grams
13	600 grams	353 grams	191 grams
14	603 grams	359 grams	188 grams
15	603 grams	353 grams	194 grams
16	603 grams	357 grams	190 grams
17	602 grams	353 grams	193 grams
18	578 grams	330 grams	192 grams
19	592 grams	338 grams	198 grams
20	594 grams	348 grams	190 grams
Range	574 - 608	330 - 361	174 - 198
Average	592	349	187

Boot #	Total Boot Weight	Upper Weight	Outsole Weight
21	602 grams	357 grams	189 grams
22	583 grams	347 grams	180 grams
23	583 grams	344 grams	183 grams
24	590 grams	347 grams	187 grams
25	596 grams	355 grams	185 grams
26	590 grams	344 grams	190 grams
27	567 grams	334 grams	177 grams
28	574 grams	342 grams	176 grams
29	593 grams	342 grams	195 grams
30	594 grams	344 grams	194 grams
31	583 grams	335 grams	192 grams
32	589 grams	347 grams	196 grams
33	594 grams	343 grams	195 grams
34	574 grams	334 grams	184 grams
35	587 grams	346 grams	185 grams
36	594 grams	351 grams	187 grams
37	597 grams	345 grams	196 grams
38	579 grams	350 grams	173 grams
39	593 grams	340 grams	197 grams
40	589 grams	338 grams	195 grams
	567 - 602	334 - 357	173 - 197
	588	344	187

Boot #1 - 20 --------- Panama design outsole
Boot #21 - 40 -------- Chevron design outsole

TABLE V

DATA APPLICABLE TO THE FIFTY PAIR OF COMBAT BOOTS (PHASE II)

BOOT #	TOTAL BOOT WEIGHT GRAMS	UPPER WEIGHT* GRAMS	OUTSOLE WEIGHT GRAMS	SPECIFIC GRAVITY	SHORE A HARDNESS HEEL	SHORE A HARDNESS TOE	POLYAIR FLEXER AT 15000 BENDS
1 R	643	388	255	0.69	50	50	350%
1 L	653	393	263	0.71	52	49	350%
2 R	665	409	256	0.69	51	52	no growth
2 L	630	374	256	0.69	52	52	no growth
3 R	660	405	255	0.69	52	52	350%
3 L	644	385	259	0.70	51	53	350%
4 R	631	370	261	0.70	54	53	no growth
4 L	665	404	261	0.70	52	51	no growth
5 R	665	405	260	0.70	50	53	350%
5 L	667	413	254	0.69	48	51	350%
6 R	649	394	255	0.69	50	54	no growth
6 L	671	418	253	0.69	52	52	no growth
7 R	665	411	254	0.69	52	52	400%
7 L	672	416	256	0.69	50	50	400%
8 R	670	411	259	0.70	52	50	150%
8 L	655	400	255	0.69	53	52	150%
9 R	665	404	261	0.70	53	52	no growth
9 L	640	385	255	0.69	48	49	no growth
10 R	630	383	247	0.66	55	55	no growth
10 L	650	400	250	0.68	49	49	no growth
11 R	643	395	248	0.66	52	51	100%
11 L	662	408	254	0.69	48	52	100%
12 R	645	394	251	0.68	49	52	100%
12 L	660	406	254	0.69	52	51	100%
13 R	628	373	255	0.69	54	53	no growth
13 L	650	390	260	0.70	51	51	no growth
14 R	634	378	256	0.69	52	53	150%
14 L	624	368	256	0.69	50	50	150%
15 R	640	384	256	0.69	52	52	150%
15 L	624	365	259	0.70	48	48	150%
16 R	639	382	257	0.69	48	50	50%
16 L	664	406	258	0.69	52	51	50%
17 R	663	406	257	0.69	49	51	150%
17 L	645	397	248	0.66	49	49	150%
18 R	632	374	258	0.69	54	52	no growth
18 L	636	385	251	0.68	50	50	no growth
19 R	676	419	257	0.69	52	51	no growth
19 L	668	408	260	0.70	50	51	no growth
20 R	640	385	255	0.69	55	53	no growth
20 L	647	385	262	0.70	49	48	no growth
21 R	617	385	232	0.63	50	49	no growth
21 L	661	405	256	0.69	47	46	no growth
22 R	624	370	254	0.69	55	53	100%
22 L	654	396	258	0.69	49	50	100%
23 R	670	398	257	0.69	51	53	no growth
23 L	655	409	256	0.69	50	51	no growth
24 R	653	394	259	0.70	48	52	no growth
24 L	640	383	258	0.70	47	50	no growth
25 R	638	382	256	0.6[illegible]	50	54	no growth
25 L	675	414	261	0.70	52	52	no growth

TABLE V

DATA APPLICABLE TO THE FIFTY PAIR OF COMBAT BOOTS (PHASE II)

BOOT #	TOTAL BOOT WEIGHT GRAMS	UPPER WEIGHT* GRAMS	OUTSOLE WEIGHT GRAMS	SPECIFIC GRAVITY	SHORE A HARDNESS HEEL	SHORE A HARDNESS TOE	POLYAIR FLEXER AT 15000 BENDS
1C R	584	376	208	0.56	40	38	600%
1C L	597	394	203	0.55	35	38	600%
2C R	616	408	208	0.56	36	40	600%
2C L	605	406	199	0.54	33	37	no growth
3C R	604	396	208	0.56	34	38	800%
3C L	604	396	208	0.56	33	34	800%
4C R	580	376	204	0.55	40	44	no growth
4C L	586	384	202	0.55	35	37	no growth
5C R	604	393	211	0.57	36	43	300%
5C L	598	390	208	0.56	35	40	300%
6C R	591	381	210	0.57	35	38	800%
6C L	600	392	208	0.56	33	35	800%
7C R	584	372	212	0.57	36	36	800%
7C L	621	410	211	0.57	33	34	800%
8C R	632	420	212	0.57	35	39	600%
8C L	597	389	208	0.56	33	35	600%
9C R	591	382	209	0.57	34	35	no growth
9C L	595	386	209	0.57	32	33	no growth
10C R	581	376	205	0.55	34	40	800%
10C L	591	384	207	0.56	31	33	800%
11C R	614	405	209	0.56	34	40	800%
11C L	595	383	212	0.57	34	36	800%
12C R	582	375	217	0.56	32	35	no growth
12C L	580	376	204	0.55	31	33	no growth
13C R	601	390	211	0.57	38	42	no growth
13C L	621	412	209	0.56	36	38	no growth
14C R	598	392	206	0.55	36	45	no growth
14C L	619	410	209	0.56	36	41	no growth
15C R	600	390	210	0.57	37	40	no growth
15C L	611	400	211	0.57	34	38	no growth
16C R	571	358	213	0.57	37	44	300%
16C L	593	385	208	0.56	34	39	300%
17C R	590	380	210	0.56	36	43	no growth
17C L	595	384	211	0.56	35	38	no growth
18C R	589	379	210	0.56	37	43	150%
18C L	597	385	213	0.57	34	36	150%
19C R	613	400	213	0.57	38	44	no growth
19C L	610	400	210	0.57	34	40	no growth
20C R	605	396	209	0.56	37	41	no growth
20C L	601	399	202	0.55	33	39	no growth
21C R	604	391	213	0.57	38	42	no growth
21C L	594	383	211	0.57	35	37	no growth
22C R	582	371	211	0.57	38	42	200%
22C L	601	392	209	0.57	32	36	200%
23C R	599	387	212	0.57	35	40	no growth
23C L	597	388	209	0.56	34	41	no growth
24C R	595	391	204	0.55	37	44	no growth
24C L	593	385	208	0.56	36	42	no growth
25C R	629	418	211	0.57	39	41	no growth
25C L	614	404	210	0.57	34	38	no growth

* Includes weight of leather upper, heel plug, shank, and hot melt adhesive.

VI. CONCLUSIONS

1. The fabrication of an abrasion-resistant, 0.55 specific gravity closed-cell outsole is feasible on a Polyair liquid injection machine.

2. The availability of Polyair LIM equipment provides an excellent means to mass produce lightweight polyurethane outsoles.

3. The use of a Polyair flex tester is an excellent means of quality control.

4. The premature flex cracking of outsoles was eliminated. The cause of outsole flex cracking was attributed to:

   a) improper metering of compound when using a 100 to 10 weight ratio of prepolymer to curative, a ratio which must be accurately metered.

   b) improper mixing of compound when using a low speed mixer and a combination of high viscosity prepolymer and low viscosity curative.

   c) integral skinned foam where skin thinness was located in high stress areas of the outsole.

   Steps taken to eliminate the flex cracking were as follows:

   a) the use of a quasi-prepolymer technique (70 to 100 weight ratio of prepolymer to curative) on a Polyair LIM to minimize the need for very accurate metering.

   b) improvement of mixing was improved by using lower viscosity materials and a high speed (1800 RPM) mixer.

   c) reduction of flex failures in high stress areas by use of a uniform density outsole.

   d) use of lower processing temperatures (110 - 120°F) to minimize the need for accurate control of high temperatures.

5. The development of the modified chevron outsole design may also aid in eliminating flex cracking of the outsoles.

ACKNOWLEDGEMENTS

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LIST OF MATERIALS

MATERIAL (TRADE NAME)	CHEMICAL NAME	SOURCE
Dabco	triethylenediamine	Houdry Co.
3041 Black	furnace black, dispersed in DOP	Inmont Corp.
1,4 butanediol	1,4 butanediol	GAF Corp.
DC 193	silicone surfactant	Dow Corning Corp.
mPDA	meta phenylene diamine	Miller-Stephenson Chemical Co., Inc.
Methylene chloride	methylene chloride	Hubbard-Hall Chemical
MDI	4,4' diphenylmethane diisocyanate	Mobay Chemical Co.
Multrathane F222	polyester polyol	Mobay Chemical Co.
Multrathane R14	polyester polyol	Mobay Chemical Co.
Nitrosan	N,N'-dinitroso - N,N' dimethyl terephthalamide	E.I. DuPont DeNemours & Co., Inc.
Santicizer S-160	butyl benzyl phthalate	Monsanto Chemical Co.
T-9	stannous octoate	M&T Chemical Co.
TDI	tolylene diisocyanate	Upjohn Co.
US-1SN	secondary plasticizer	East Coast Chemical
Vibrathane B-600	polyether, urethane polymer	UniRoyal Chemical Div.
Vibrathane B-602	polyether, urethane polymer	UniRoyal Chemical Div.
Vibrathane B-605	polyether, urethane polymer	UniRoyal Chemical Div.