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TECHNICAL REPORT 6712

DEVELOPMENT OF FOAMED ACRYLATE-AMIDE TERPOLYMER

PROGRESS REPORT #3, SUMMARY REPORT

Reported by

C. A. Nielson

November 1967

U.S. ARMY MEDICAL BIOMECHANICAL RESEARCH LABORATORY
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ABSTRACT

This report covers the additional work that was done under Subtask 23, Tissue Repair and Replacement, under Project 6-59-12-022, Traumatic Surgery and Shock, leading to the improvements in the processing of foamed latex as they apply to the latex produced at the U.S. Army Medical Biomechanical Research Laboratory.

I. INTRODUCTION

Continued interest in the acrylate-amide terpolymer as a biostable tissue substitute and repair material, and the requirement that for some applications it needs to be in the form of a sponge or foam, stimulated efforts to improve the reproducibility of the process for its manufacture.

This report deals with a summary of the innovations that were introduced to improve the stability, viscosity and general processing characteristics of the latex and foamed products therefrom and applies only to the latex prepared at this laboratory.

II. PROCEDURE

The terpolymer was prepared by emulsion polymerization according to the procedure of Leonard, et al.[1] with the exception that 2.5 parts of surfactant were used and 1.0 part of polyvinyl alcohol (Elvanol [2] 71-30) was added to the recipe.

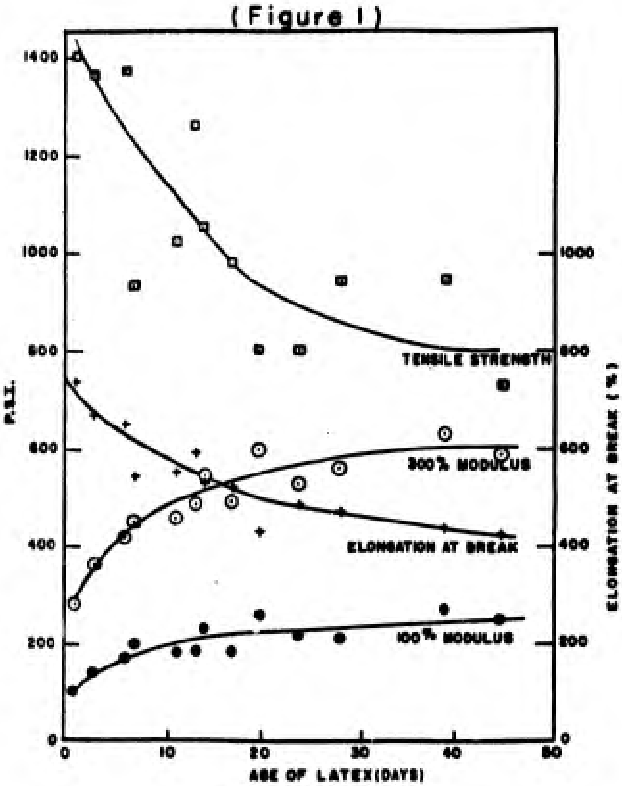
The following was a typical polymerization run:

Ingredients	Parts
Butylacrylate (distilled)	90
Methylmethacrylate (distilled)	7.5
Methacrylamide	2.5
Water (demineralized)	155
Santomerse SX	2.5
Elvanol 71-30	1.0
Potassium chloride	0.344
Potassium persulfate	0.024
Sodium thiosulfate	0.0177
Sulfuric acid	0.0625
Temperature 25°C, pH 2.5	

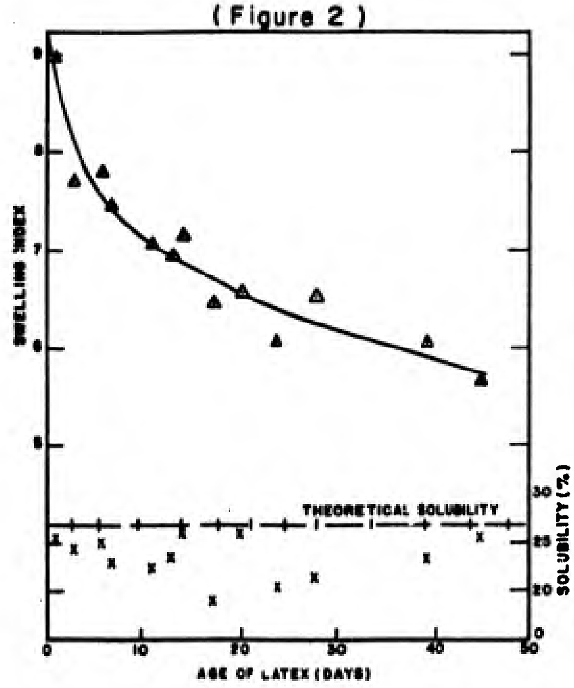
To this emulsion was added 37 parts by weight, based on the solid terpolymer content, of polyethyl methacrylate from an emulsion thereof, together with 1.765 parts formaldehyde added as formalin.

Even with the addition of polyvinyl alcohol to the polymerization recipe, the latex was still somewhat sensitive to the addition of compounding ingredients. This was especially true of the freshly compounded latex and to a lesser degree with latex that has undergone a period of aging. The change in compounding characteristics appears to be associated with the degree of crosslinking, as are some of the other properties, Fig. 1, physical and Fig. 2, chemical.

(Figure 1)



(Figure 2)



This behavior of the latex to compounding was overcome by resorting to accelerated aging wherein the latex was subjected to a period (3 hours) of heating at 95°C in a reaction vessel equipped with a condenser and stirrer. Stability of the latex toward subsequent compounding was thusly insured.

The original foam recipes[3, 4, 5] were changed by substituting WS 851[6] for the other thickening agents. This product is ammonium polyacrylate having an average molecular weight of 250, 000 and it is a gel free solid. In use, latex viscosities can be regulated and repeated from batch to batch without any difficulty so long as the thickening is accurately measured from a known solution by means of a graduated hypodermic syringe.

A 15% solution of this agent has a pH of 5. 7, practically neutral. This is advantageous because it may be added to the latex without the necessity for pH adjustment. Such was not the case with other thickening agents whose pH would range upwards toward 12. 0. It also took a great deal less of this new product to achieve comparable viscosities and a smoother, more homogeneous emulsion resulted.

The other modification that was made in the foam recipe was in the change of base from ammonium hydroxide to triethanolamine. This was done for several reasons: the variableness of concentration of NN_4OH through loss of NH_3 by volatilization; its susceptibility to combination with both the citric acid and the formaldehyde forming ammonium citrate and hexamethylenetetramine respectively; difficulty in controlling the drop-wise addition of it and the objection to its presence in the atmosphere by the operators.

A much better control was obtained by the use of a 25% solution of triethanolamine (v/v), pH 10. 1. Here again, the amount required was easily measured accurately with a graduated syringe and the effect of this base on setting time was not as critical as when ammonium hydroxide was used. Adjustments in the amount of this ingredient were usually only necessary to compensate for unusual differences in temperature.

The following is the revised compounding formulation:

Ingredients	pH	Amounts
X-10-E latex (USAMBRL)	3.9-4.0	200.0 cc/org.
1-N citric acid	1.8	6.0 cc
Ammon.polyacrylate (WS-851) 15%	5.7	1.5 cc ± 0.5
Triethanolamine 25%	10.1	3.0 cc ± 0.5
Sodium fluorosilicate (50% suspension)	7.4	2.0 g ± 0.5
Final pH at set point of batch	7.4	

The amount of this recipe can be increased for larger batches.

To prepare the mixture, the first 3 ingredients were blended in the order given in the mixing equipment at a slow speed until a smooth homogeneous mix resulted. For a guide to this speed, the number 3 setting on a Sunbeam Mixmaster (number scale) could be used. Triethanolamine was then added and mixer speed increased to that represented by the number 7 setting and maintained until a three-fold rise in foam volume had been achieved. A thin slurry of the setting agent(Na_2SiF_6) containing 2 or 3 drops of 18% Santomerse SX was poured into the mixture. Stirring speed was reduced to that of the point 4 setting, the mixing bowl was kept turning and a flexible rubber scraper blade applied to the sides of the bowl so as to bring the foam on the sides into the stirring mix. 45 seconds were allowed for the mixing of the setting agent from the time that it was added.

From 1-1/2 to 2 minutes were considered to be sufficient for the final solidification of the foamto take place. From the time that the setting agent had been added, there was a brief period during which the foam was in a fluid state, although it became progressively more viscous from the effect of the sodium fluorosilicate. This is the period or working time during which the foam can be manipulated. After that, nothing can be done without breaking the cell structure. It is important in most cases to accomplish the intended work within as short a period as possible in order to preserve the uniform character of the foam structure. A prolonged setting time causes coalescing of cells, which if desired to obtain a foam with larger cell structure can be obtained in this way, but is usually to be avoided.

One of the most serious objections to the original foam recipe, aside from its erratic and difficult processing characteristics, was its prolonged weak wet strength after final set. It was necessary to handle the foam with extreme care. After foaming, it had to be stored for long periods under conditions of high humidity before it was safe to handle it. Rejects of 50% or more were not unusual and, in some instances, a foam could not be made at all.

Fig. 3 shows graphically the rates at which the two foams develop wet strength from the time they have acquired permanent set onwards. In this test, foamed sheets were prepared that were 1/4 inch thick. A determination of the maximum load that each could bear was made by placing an aluminum disc 1-1/8 inch in diameter and weighing 1.4 gram carefully on the sheets of foam with added weights at 10 minute intervals. The rapid development in strength or ability to support loads by the foams of the new recipe was a most desirable characteristic. Foamed items could now be exposed to accelerated drying and curing without risk of failure, thus making the process economically feasible.

Fig. 4, samples A. B, C, D, were cut from foams made from the original recipe. Sample E was taken from a sheet made from the new formula but without the citric acid. Sample F represents an example from the new complete formula.

III. SUMMARY

Certain changes and substitutions have been made in the original formula for making the foamed form of the acrylate amide terpolymer elastomer that have resulted in greater latex stability, easier processing, reliability and reproducibility. A new formula has been presented, together with instructions for its use. While it is presently limited to the latex manufactured at the U.S. Army Medical Biomechanical Laboratory, there appears to be no reason why the same product cannot be duplicated in industry, and on a larger scale, if the same procedure is adhered to for preparing the latex and making the foam.

Additional surfactant was added to the polymerization recipe. Polyvinyl alcohol was employed in the polymerization recipe instead of using it as a later additive. Accelerated aging was accomplished by heating the compounded latex, thereby bringing about earlier crosslinking which made the latex receptive to compounding ingredients without the risk of coagulating the latex. A very considerable increase in the initial wet strength of the foam was responsible for reducing the number of rejects to a very significant extent. Using this formulation, it has been possible to prepare satisfactory foams in all cases.

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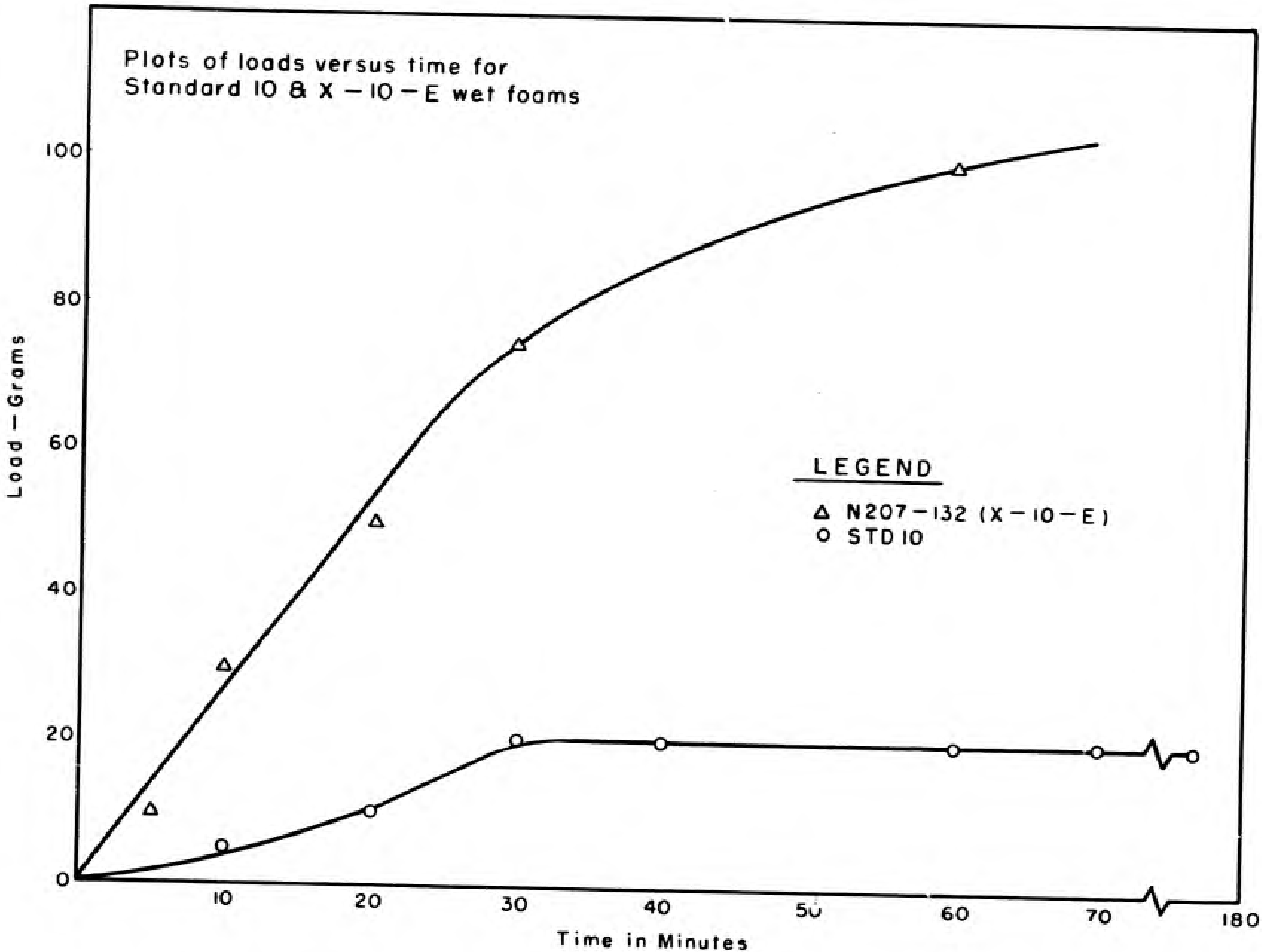

Plots of loads versus time for
Standard 10 & X – 10 – E wet foams
Load – Grams
0
20
40
60
80
100
10
20
30
40
50
60
70
180
Time in Minutes
LEGEND
△ N207–132 (X – 10 – E)
○ STD 10

(Figure 3)

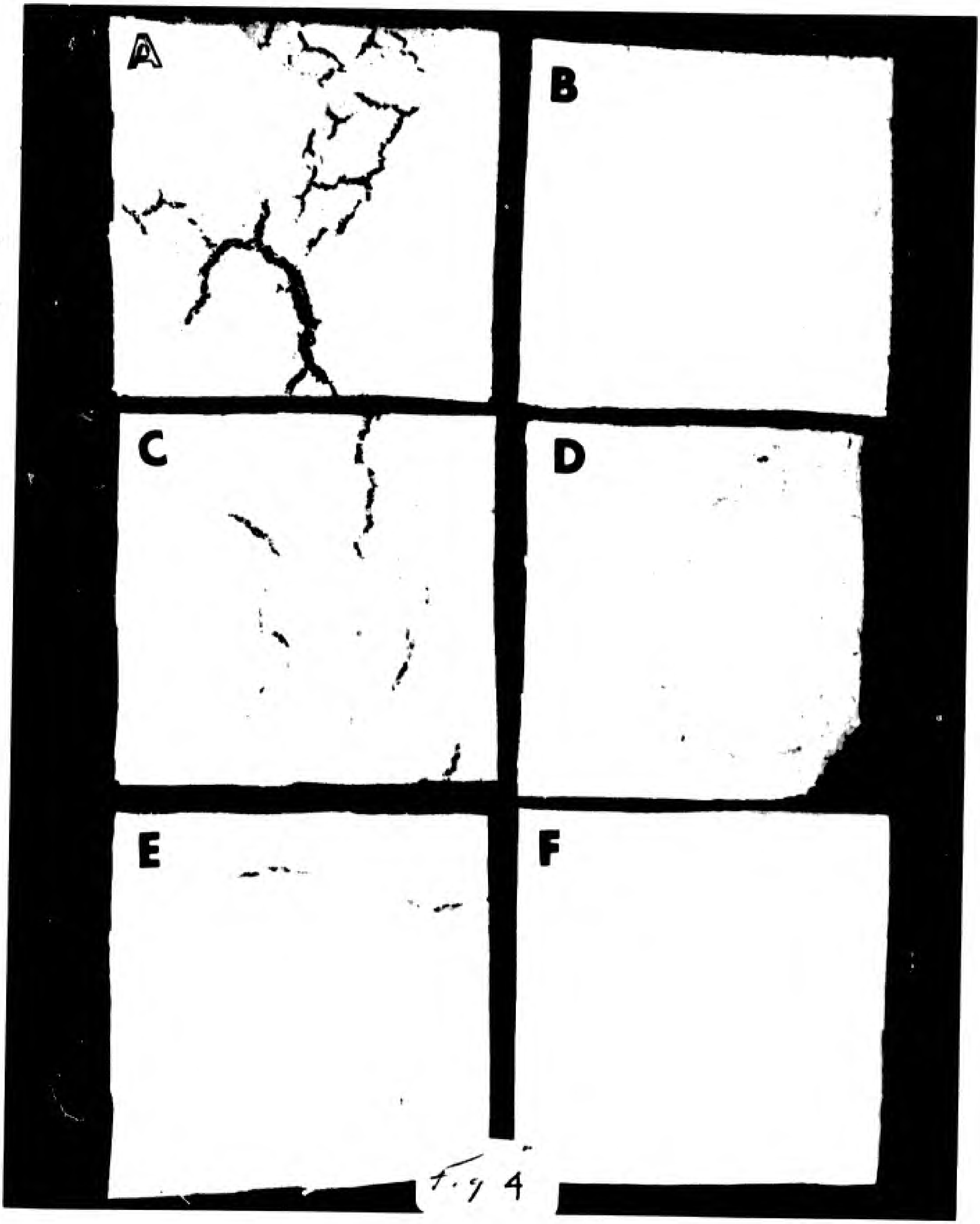

Fig 4

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Foam						
Acrylate terpolymer						
Polyvinyl alcohol						
Ammonium polyacrylate						
Triethanolamine						
Reproducibility						