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CHEMISTRY DIVISION - HIGH POLYMER SECTION

3 December 1945

FR-2691

CELLULOSE CAPRATE CEMENT

By H. A. Tanner, A. Rogovin and
L. Lockhart

\- Report P-2691 -

[redacted]

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Director, Naval Research Laboratory

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ABSTRACT

This report describes the development of a new lens cement for optical elements. The cement finally chosen was cellulose caprate. This ester is manufactured by the Eastman Kodak Company and must be purified before use. Details of purification, methods of application and results obtained with its use are given.

TABLE OF CONTENTS

AUTHORIZATION

1. This project was authorized by the Bureau of Ordnance letter to the Naval Research Laboratory, (Re4e) NP14 of 21 November 1944.

STATEMENT OF PROBLEM

2. Due to the extreme temperature conditions encountered by the Navy during World War II in operations all over the world, numerous failures of optical instruments were observed. These failures were caused in many instances by the available optical cements' inadequacy at both high and low temperatures.

3. Two general types of cements have been used, thermoplastic and thermosetting. Those of the first class have had several drawbacks; either they became soft at temperatures slightly above normal and allowed the doublets to slip relative to one another, or they were too viscous to apply at reasonable temperatures and became brittle at low temperatures. The second class also had many disadvantages. They were not stable over long periods of time, they required special techniques in their use, they caused excessive amounts of strain in the optical elements, they did not withstand service use and doublets cemented with them could not be conveniently separated when repair was necessary.

4. The problem as presented to the Naval Research Laboratory was the development of a new cement for optical elements which did not have the disadvantages enumerated above. As a guide for the properties desired, the Naval Research Laboratory made use of a list of the properties of an ideal cement which were compiled by the Optical Shop of the Naval Gun Factory, Washington, D. C., in conjunction with Frankford Arsenal of Philadelphia, Pennsylvania. The properties desired were the following:

(a) Substantially colorless and neutral in light absorption.
(b) Clear and non-scattering.
(c) Refractive index between 1.51 and 1.58, preferably 1.52 to 1.54.
(d) Chemically neutral to glass; that is, no leaching or other destructive effect upon glass surfaces.
(e) Good adhesion to glass with sufficient flexibility and mechanical properties such that adhesion and clarity are unaffected by indefinite storage at any temperature between -60°F and +160°F. At 160°F the cement must be capable of withstanding a shear of five ounces per square inch of cemented surface.
(f) If the cement is to be polymerized between the lens elements it should be capable of polymerizing with a minimum amount of shrinkage and if possible at room temperature. The use of high temperatures should be avoided.
(g) Sufficiently stable to ship and store for approximately a month before use and should be shippable ready for use or

at least in such form that the user will have a minimum number of simple operations to perform before applying them.

(h) Good aging characteristics so that upon indefinite aging or storage within the required temperature range it does not lose its adherence to glass or become yellow. This should include resistance to moderate amounts of ultraviolet light.

(i) It should be fungistatic, preferably fungicidal.

(k) Substantially non-toxic.

(l) The materials should permit separation of optics when necessary with low breakage hazard. This includes ease of removal of cement from the glass.

(m) No effect on optical properties of component elements (e.g. straining or surface distortion).

(n) The cement at the time of application should be sufficiently fluid to permit cementing at a temperature of 250°F or lower.

5. The problem, therefore, was to develop a cement fulfilling the above requirements.

KNOWN FACTS BEARING ON THE PROBLEM

6. The cement must be a transparent continuum and will therefore be in the nature of a glass, plastic, resin, wax or rubber. In order to maintain a bond over the wide temperature range required, the cement must have a thermal coefficient equal to that of optical glass or it must have a certain amount of plasticity. These considerations rule out resins since they are brittle at low temperatures and do not have the proper thermal coefficients. This is the reason that balsam cement will not withstand low temperatures. Waxes, likewise, become brittle at low temperatures and tend to crystallize. With inorganic glasses the strength of adhesion is low and the materials are brittle. The thermal coefficients must therefore be exactly equal. Since the principle application of optical cement is between two kinds of glass having different thermal coefficients, this becomes impossible and glasses can be eliminated from further consideration.

7. An optical cement must at the time of application be a fairly thin liquid at a temperature not exceeding 250°F and it must, after application, be a rigid solid at 160°F. Either the material must melt rather sharply between 160°F and 250°F or it must, after application, undergo some chemical transformation (such as polymerization) which will raise the melting point above 160°F. The only chemical transformations possible in a confined space, as between lens elements, which will not produce by-products tending to cause haze and opalescence, are the reactions of vulcanization and polymerization. In these reactions small molecules unite to form large molecules with a resultant decrease in volume. In the case of polymerization of monomeric materials, this volume shrinkage usually exceeds 10%. Vulcanization, or the joining of molecules by cross linkages, involves starting with rather high molecular weight materials (rubbers) which are too viscous, even before reacting, to be usable as lens cements by the present techniques.

8. The use of polymerization or vulcanization is a definite possibility for preparing a satisfactory cement. The shrinkage factor would have to be balanced by some plasticity in the final product and diminished through partial polymerization before use or by starting with fairly high molecular weight materials. None of the presently available polymerizable or vulcanizable materials are satisfactory. The use of such a cement would require skill and technique and it would require either the handling and storage of a chemically unstable mixture or the preparation of such a mixture immediately prior to use.

9. Certain polymerizing-type cements are in use at present. These have proven unsatisfactory because the shrinkage during polymerization exceeds the plasticity of the polymer causing strains and distortion of elements and a certain percentage of failures upon aging. A further disadvantage of these cements is the difficulty of separating elements after the cement has polymerized.

10. From the above considerations it is concluded that while a satisfactory polymerizing or vulcanizing cement is possible, a more promising line of attack for immediate results is in the use of a thermoplastic material meeting the melting point requirements of paragraph 7. This material will of necessity be plastic in nature, but may contain as modifying agents, resins, waxes, rubbers, and liquid or solid plasticizers.

ORIGINAL WORK DONE

11. The most difficult requirement to meet with a thermoplastic cement is the sharp melting point. Thermoplastic materials ordinarily soften and melt over a very wide temperature range, so that either they will lack permanent rigidity (lack of cold flow) at 160°F or they will not melt to a thin liquid below 250°F. There are the following possible methods of obtaining a thermoplastic cement having the proper melting characteristics:

(a) A mixture of a thermoplastic with a liquid or solid having such solvent action that the mixture transforms from a rigid gel to a thin solution at some temperature between 160°F and 250°F.
(b) A mixture of a thermoplastic with a resin in order to combine the sharp melting characteristics of the resin with the low temperature plasticity of the thermoplastic.
(c) An unmodified thermoplastic substance of proper melting point and low molecular weight so that a thin liquid will be formed on melting.

12. Thermoplastic mixtures consisting of a thermoplastic substance plus one or more resins, or liquid or solid plasticizers, or both are an obvious lines of attack on this problem and are known to have been studied extensively. A satisfactory plasticizer would have to fulfill the solubility characteristic of paragraph 11(a) because otherwise, there is no hope of obtaining a melt below 250°F which will not cold

flow at 160°F. The usual action of a plasticizer is to decrease the zero cold flow temperature more than it decreases the melting point. A great number of thermoplastic-plasticizer mixtures were made and tested. (Table I). All of these mixtures were found to have several objectionable features. There is a tendency for the plasticizer to exude at low temperatures causing opalescence and diminished adhesion. Such mixtures when placed on an optical element lose plasticizer by evaporation during melting resulting in a non-uniform cement. Plasticizers tend to be lost through evaporation over a period of time resulting in poor aging characteristics.

13. Mixtures of a thermoplastic with a resin (Table II) were also investigated extensively. In general it was found that if sufficient resin were added to give a thin melt at 250°F either there was cold flow at 160°F, or failure at low temperatures, or both.

14. As all of the results obtained with methods (a) and (b) of paragraph 11 were negative, efforts were concentrated on (c) and a search made for an unmodified thermoplastic substance with the proper melting point. Most of the commercially available thermoplastic materials either melt too high or show cold flow at 160°F. The following materials come nearest to fulfilling the requirements and were examined for their possible use as a lens cement:

Ethyl cellulose	low viscosity 48% ethoxyl
Butyl cellulose	low viscosity
Benzyl cellulose	low viscosity
Polyvinyl acetate	low viscosity
Polyvinyl benzoate	low viscosity
Polyvinyl ethyl ether	low viscosity
Low melting saran type polymers	
Agar benzoate	
Low melting nylon	
Polystyrene	low viscosity
Acetate of hydroxyethyl cellulose	
Benzoate of hydroxyethyl cellulose	
Low viscosity cellulose esters of the higher fatty acids.	

All of the above materials passed the low temperature requirement and most of them either showed no cold flow at 160°F or melted to a thin liquid below 250°F. The only materials which gave zero cold flow at 160 F and melted to a thin liquid at 250°F were the cellulose esters of the higher fatty acids.

15. A more careful examination of the cellulose esters available showed that those esters of ten to eighteen atoms seem to give satisfactory results. The character of the melt at 250°F was determined for the following esters with the results indicated: cellulose caproate, viscous and rubbery (2 samples), cellulose caprate, satisfactory (7 samples), slightly viscous (1 sample), cellulose laurate, satisfactory (1 sample), viscous (1 sample), cellulose stearate, satisfactory (1 sample), viscous (1 sample), and cellulose butyrate-stearate, viscous (1 sample). These preliminary results show that the caprate had

the most possibilities. However, as received, the material was too dirty and impure to be used in lenses.

Purification of Caprate

16. Cellulose caprate is produced by the Eastman Kodak Company as a granular powder. The material as received is subjected to a 48 hour extraction in a Soxhlet apparatus (Plate I) using a methanol-water mixture 80/20. This extraction removes the oily impurities, presumably a mixture of unreacted capric acid and other oily-like materials collected during manufacture. After this extraction, the ester is dried at room temperature and then dissolved in toluene, 15 grams per 100 cc. and filtered. The filtration consists of three passes through a medium sintered glass filter with the aid of suction, three passes through a fine sintered glass filter, and finally, one pass through a fine filter into the apparatus used for casting sticks. (Plate 2). The toluene is evaporated at reduced pressure by placing this apparatus in an oil bath maintained at 110°C. (Plate 3). When all the toluene has been removed and the air bubbles have risen to the surface, the material is removed from the oil bath and allowed to solidify. A glass rod is heated on one end, inserted to a depth of about an inch into the caprate and allowed to cool. The entire assembly is then placed in an oil bath at 120-130°C for 70-80 seconds and the stick of cement pulled free. The purified cellulose caprate cement as prepared above is a tough, flexible material with a waxy feel. The color will range from practically water-white to a light amber, depending upon the extent of purification. This material is permanently thermoplastic. It is soluble in most organic solvents and unaffected by water. It is non-toxic and causes no deterioration of glass.

Tests and Results

17. Many preliminary tests were made on the cellulose caprate as prepared above merely as a quick evaluation of the product and do not necessarily represent what happens in a lens, but were required for comparison with balsam.

18. The melting point of this material depends on the method of measurement and on the viscosity. The samples prepared for an optical cement melt in the range of 90-95°C with most of the material melting at 95°C when determined by the method of Durrans. This method is the one in which a small amount of the material is melted in the bottom of a test tube, cooled, then covered with mercury and warmed until the material floats to the top of the mercury.

19. The melting point is of less importance than the fluidity of the melt at 250°F and the lack of cold flow at 160°F. As a simple method of determining the fluidity of the melted cellulose caprate, a 15 mm x 125 mm test tube was filled half full with granular purified cellulose caprate and placed in a 125°C oil bath. After five minutes the material has melted and run down to form a melt in the bottom of

the tube. A good many thermoplastics melt at 100°C or less but very few will have sufficient fluidity at 130°C to pass the above test.

20. Further information on the fluidity of the melted caprate was obtained by comparing the rate of slippage of flat discs under various loads and at various temperatures using caprate cement and balsam cement. The results indicated that the caprate at 250°F would have about the same viscosity as balsam at 215°F.

21. Cellulose caprate is essentially an inert material which will not deteriorate in storage if properly made. A good index to the stability of the material is provided by the "char point", or temperature at which the material begins to char. Materials with a high char point have good stability. The char point of cellulose caprate can be expected to be above 250°C.

22. The stability at high and low temperatures was determined by holding cemented discs at 170°F for three weeks followed by -70°F for three weeks. The caprate is unaffected by this treatment.

23. The effect of ultraviolet light was determined by exposing thin films of cellulose caprate and balsam to a type S-4 sun lamp at a distance of 8 inches. After 100 hours exposure the balsam was darkened and checked, whereas the cellulose caprate was not appreciably affected. The ultraviolet transmission of the two materials was measured and it was found that while balsam absorbs below 3500 A.U. the caprate is transparent down to 2800 A.U. (Plate 4). The caprate is less affected by ultraviolet because it absorbs less light in that region.

24. The effect of moisture was determined by immersing glass discs cemented with balsam and with cellulose caprate in water at 170°F. The balsam began to fail after three days and was badly whitened and deteriorated after twelve days. The cellulose caprate was unaffected after thirty days.

25. A weathering cycle was run to determine the effect of alternate wetting and drying and the effect of ultraviolet light in the presence of moisture. This consisted in immersion of cemented discs in 120°F water for sixteen hours followed by eight hours exposure to a type S-4 sun lamp at a distance of three inches. Under this test, balsam began to separate at the edge after one cycle, began to star after two cycles, and was very badly starred, discolored and separated after three cycles. The caprate was not affected after twenty cycles

26. The strength of the caprate bond was determined by cementing together two glass discs $\frac{1}{4}$ inch thick by 2 inches in diameter This was dropped repeatedly on a cement floor from an altitude of six feet at room temperature and at -70°F with no effect other than chipping of the glass. The assembly was broken in half with a hammer and the plane of cleavage bisected the cement plane. Apparently the bond is strong enough to withstand any mechanical shock which glass will withstand.

27. The cellulose caprate bond is not affected by thermal shock. Glass discs cemented with caprate can be heated to 160°F, placed between pieces of dry ice and then reheated rapidly to 160°F repeatedly without affecting the bond.

28. Tests on optical transmission at the Optical Shop of the Naval Gun Factory showed the caprate to be neutral in light absorption. The amount of scattering will depend to a large extent on the efficiency of filtration since the caprate itself is a clear non-scattering material.

29. The refractive index of cellulose caprate was measured by the Optical Shop of the Naval Gun Factory and found to be 1.4734. While this is outside the limits first suggested, it is felt that the only effect will be a negligible increase in reflection at the cemented surfaces.

30. To obtain the final evaluation of this cement, several doublets with one surface ground flat were obtained. (Plate 5). These were cemented and the amount of strain determined with the use of an optical flat. (Plate 6). After this, the lenses were annealed at 100°C for 4 hours and re-examined. (Plate 7). They were again examined for strain and slippage after annealing for 5 hours. (Plate 8). It was found possible to remove the strain without the lens becoming uncentered.

31. The method of cementing with caprate cement is practically identical with that used for balsam; the only difference being the temperature of the hot plate. It is necessary that the temperature be raised to 135°C at the cementing surface, the cement applied as balsam, the bubbles worked out in the usual manner, the lenses transferred to a centering device, centered and placed to one side to cool. No difficulties were encountered either in cementing or centering.

32. The lack of cold flow at 160°F is one of the most difficult requirements that a thermoplastic optical cement must meet. The method of test employed at this Laboratory was to cement a lens which was then centered and annealed. The lens was then placed in an oven at 160°F and subjected to a shear force of five ounces per square inch for periods up to 96 hours. At the end of this time, the lens was again checked for centering and any displacement considered cause for rejection. In no instances did any lens cemented with caprate show any displacement at 160°F.

33. To determine the resistance of the caprate to attack by fungus, several galss discs were coated with caprate and innoculated with fungus. These plates were then placed in surroundings favorable for growth and allowed to remain for two months. At the end of this period, some growth was visible on the plates, but it was not excessive. The major effect seemed to be a surface clouding. Other samples were exposed under the same conditions for periods up to ten months and under these conditions, some growth was apparent, but by no means excessive. Cemented elements exposed under the same conditions for

ten months showed no attack whatever by fungus.

CONCLUSIONS AND RECOMMENDATIONS

Facts Established

34. It has been established that cellulose caprate will meet the following requirements outlined originally: (a), (b), (d), (e), (g), (h), (j), (k), (l), (m) and (n). The index refraction, requirement (c), of the material is 1.4734, which is too low. The fact that the index is low, is not good, but no serious difficulties are encountered. (f) does not apply. It is not fungistatic (i), and is not sufficiently fluid to permit cementing at a temperature of 250°F. (n). Ten of the requirements are met, one does not apply, three are not met. Despite the fact that this cement does not meet all of the requirements, it does offer a substantial improvement over available materials. The property of being fungistatic is not as important for Navy as for Army use, and is not considered a serious drawback. It has been learned that elements can be cemented successfully at temperatures above 250°F and therefore, this requirement is not too important. This material has one great advantage as a lens cement which was not stated in the original requirements, but is significant; that is, the method of handling. Application is the same as that used for balsam except that the hot plate must be maintained at a higher temperature. This means that no new equipment will have to be purchased for its use and that the training necessary is reduced to a minimum.

35. Our accelerated laboratory tests show that the material is superior to the currently used balsam; the one unknown factor is its action over long periods of time. Considering that the cement as developed is good enough for use, it is recommended that it be given wide service trials to determine its serviceability over long periods.

36. This problem is not closed and work will continue until a cement is obtained which meets all the requirements originally outlined.

<u>TABLE I</u>

Thermoplastic and Plasticizer Mixtures T = 150°C.

Plasticizer	Thermoplastic			
	Polyethylene	Nylon 6	Nylon 6B	Polyvinyl Benzoate
Tricresyl Phosphate	Insoluble			
Tri-p chlor phenyl phosphate	Insoluble			
Linseed oil	Swells			
Dibutyl Phthalate	Soluble, hazy rubbery gel, good adhesion	Insoluble		Soluble, soft at room temp.
Dioctyl phthalate	Soluble, gel exudes plasticizer			
Flexol 3 GH	Partially soluble, gel exudes			
Dibutyl sebacate	Soluble, gel exudes and blushes			
M 17 (Dow)	Insoluble			
Canada Balsam	Soluble, gummy mass, separates	Insoluble		Poor solubility
CR 39	Insoluble			
Balsam and dibutyl phthalate	Grainy solution, sticky gum on cooling			
2-Ethyl-hexyl sebacate	Soluble, poor gel			
Tributyoxyethyl phosphate	Insoluble			

TABLE I (Cont'd)

Thermoplastic and Plasticizer Mixtures   T = 150°C.

Plasticizer	Thermoplastic			
	Polyethylene	Nylon 6	Nylon 6B	Polyvinyl Benzoate
Stearic acid		Blushes on cooling		
2-Ethyl-hexanoic acid	Soluble, cheesy gel exudes	Soluble at 180 C, good gel and good adhesion		
Triethyl aconitate	Insoluble			
Tributyl citrate	Insoluble	Insoluble		
Diethylene triamine		Soluble, tends to crystallize, poor adhesion		
Glycerol		Soluble, gel exudes		
Ethylene glycol		Soluble, gel exudes		
Decamethylene glycol		Soluble, gel exudes and blushes		
Adipic acid		Soluble, gel exudes and blushes		
Oleic acid		Soluble, blushes on cooling	Soluble, blushes	
Rosin		Soluble, brittle cold	Soluble, brittle	

TABLE I (Cont'd)

Thermoplastic and Plasticizer Mixtures T = 150°C.

	Thermoplastic			
Plasticizer	Polyethylene	Nylon 6	Nylon 6B	Polyvinyl Benzoate
Silicone fluid 500 Series	Insoluble			Insoluble
Azelaic acid		Soluble, blushes on cooling		
Santicizer #8		Slides at 160°F		

TABLE II

Mixtures of Thermoplastics and Resins

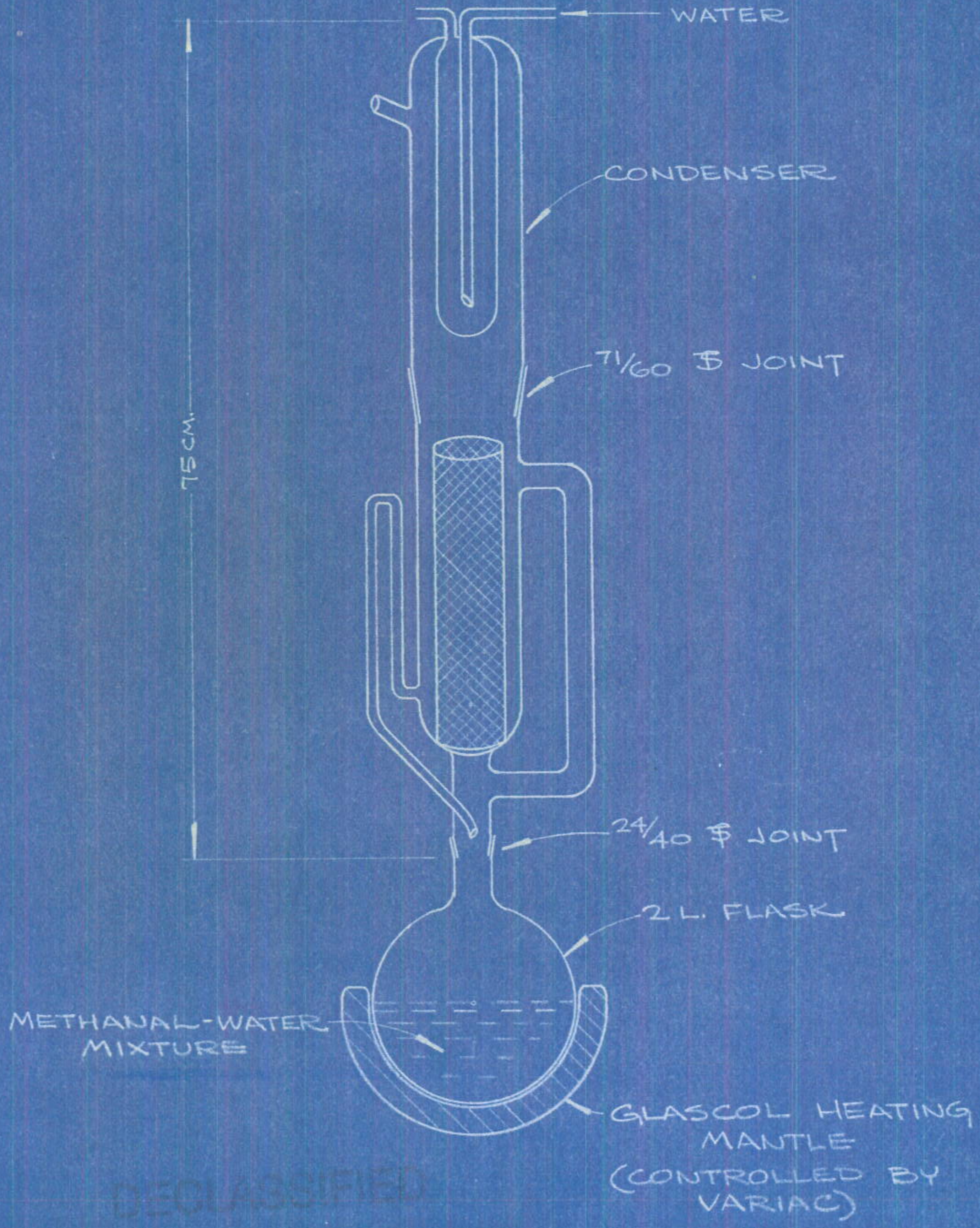
	Thermoplastics					
Resins plus Plasticizers	Polyvinyl Benzoate	Nylon Type 6B	Polyethylene	Vinylite AYAF	Vinylite AYAA	Saran X262
Canada Balsam 1:2	Separated on dry ice	Insoluble	Separated on cooling	Hazy		
Ester Gum	Separated on dry ice				Not compatible	Insoluble 1:1
BR 254	Not compatible	Crazed on dry ice			Separates on dry ice	Insoluble
Rosin		Soluble, brittle cold		Not compatible		
Beckacite 3000		Very viscous		Very viscous at 180°C	O.K. at 180°C, separates on dry ice	O.K. at 180°C, separates on dry ice
Beckacite 3000 + Dibutylphthalate				Fair	Fair	
Canada Balsam + Rosin				Hazy solution		
DBP + Rosin				Not compatible		
BR 254 + 2-Ethyl-Hexanoic Acid		Fair				

TABLE II (Cont'd)

Mixtures of Thermoplastics and Resins

	Thermoplastics					
Resins plus Plasticizers	Polyvinyl Benzoate	Nylon Type 6B	Polyethylene	Vinylite AYAF	Vinylite AYAA	Saran X262
Nevilite					Not compatible	X262 decomposed
Beckacite 3000 + 2-Ethyl-Hexanoic Acid	Viscous melt					
Rosin + 2-Ethyl-Hexanoic Acid	Fair					

SOXHLET EXTRACTION APPARATUS



EVAPORATION FLASK AND ACCESSORY HEADS

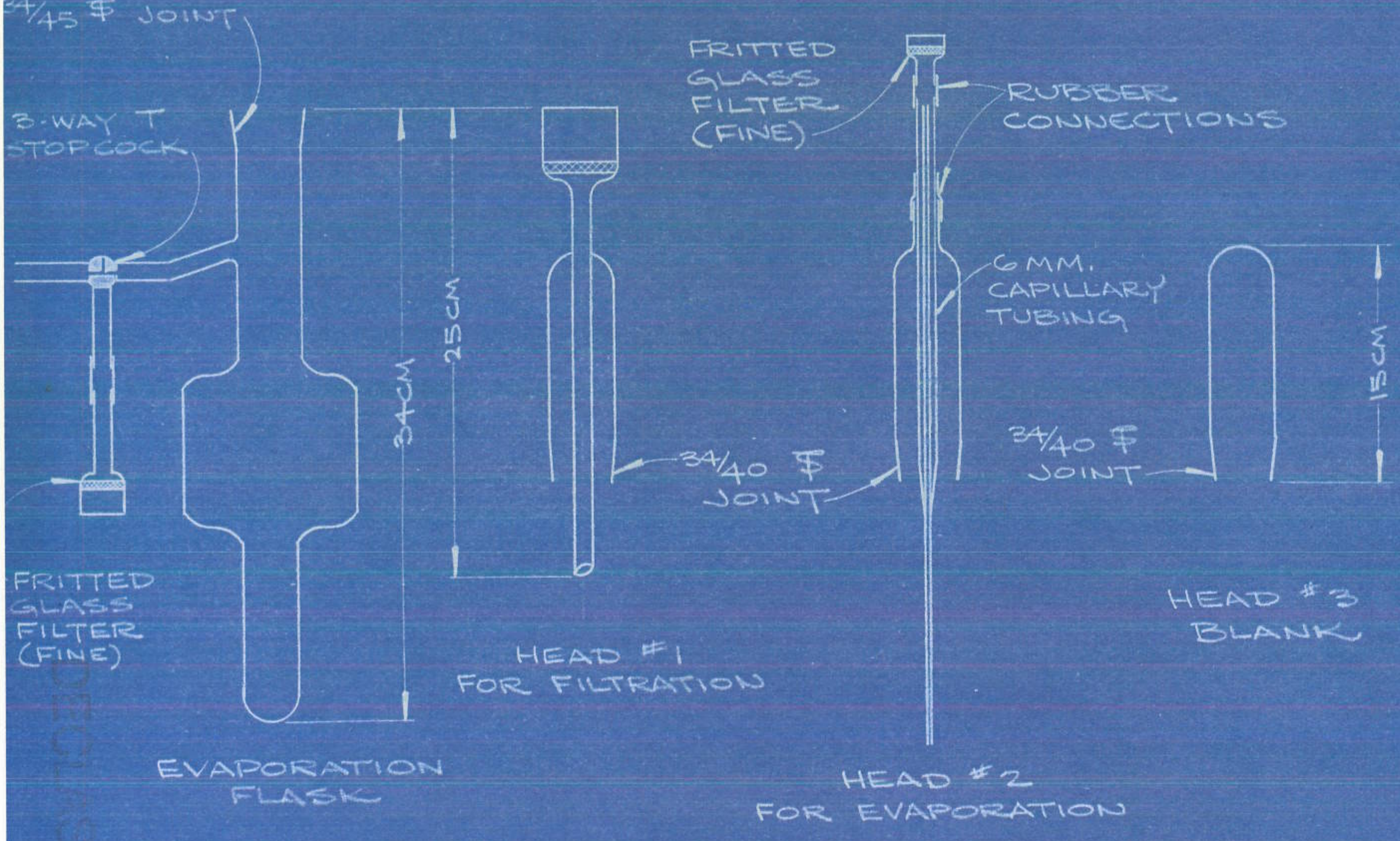
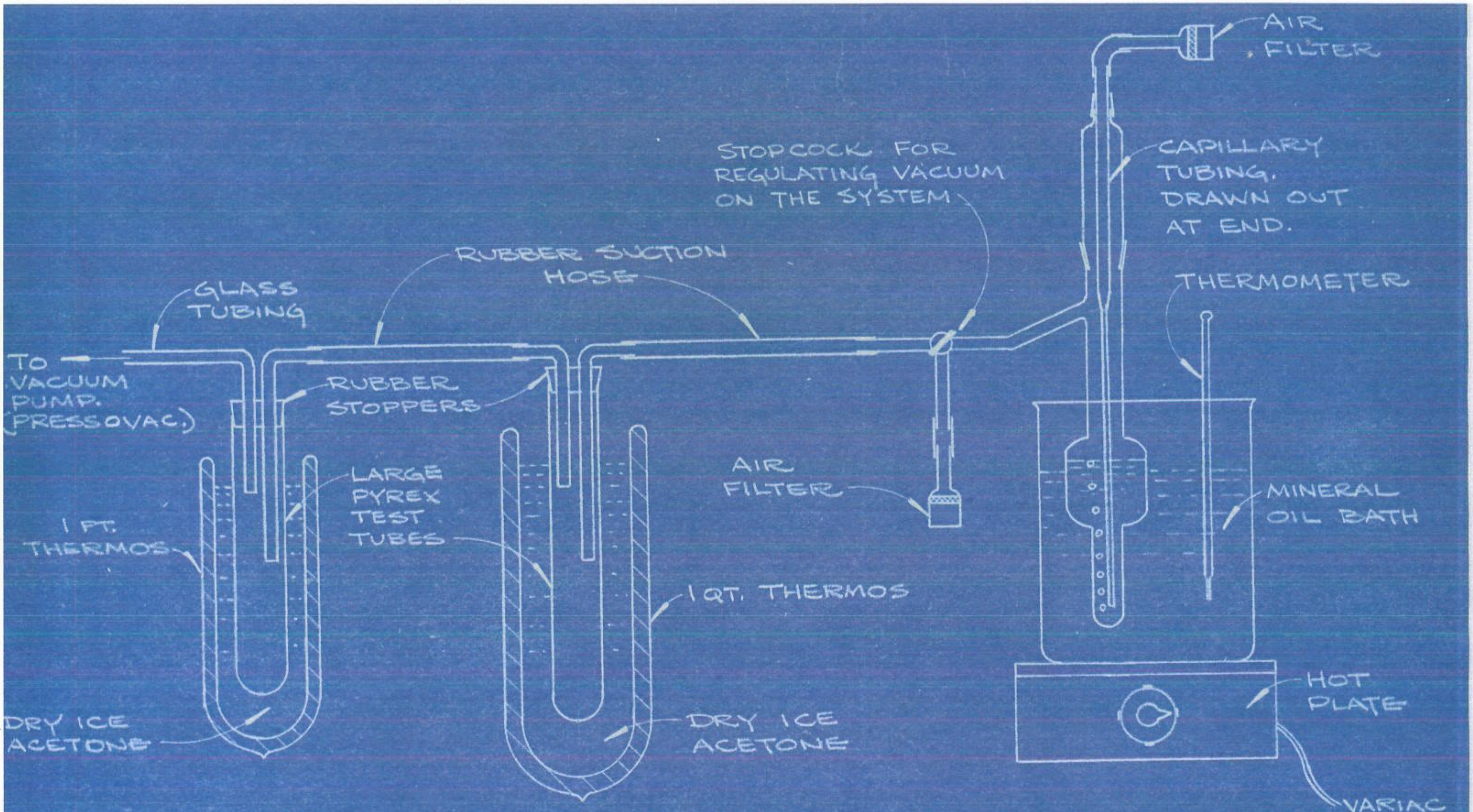
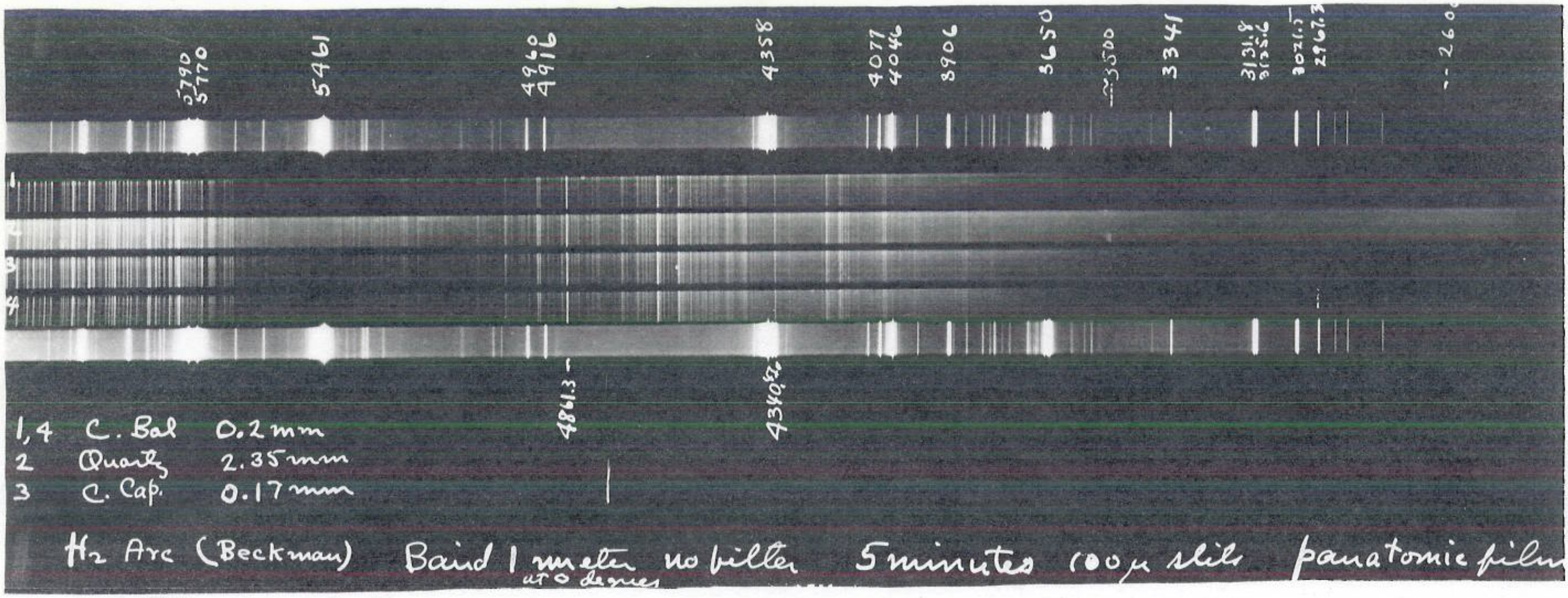


PLATE 2



APPARATUS FOR REMOVAL OF SOLVENT

PLATE 3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5770
5461
4960
4916
4358
4077
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3650
~3500
3341
3131.8
3125.6
3021.5
2967.3
-- 260
1
2
3
4
4861.3
4340.5
1,4 C. Bal 0.2 mm
2 Quartz 2.35 mm
3 C. Cap. 0.17 mm
H2 Arc (Beckman) Baird 1 meter at 0 degrees no filter 5 minutes 100μ slit panatomic film

PLATE 4

UNCEMENTED LENSES

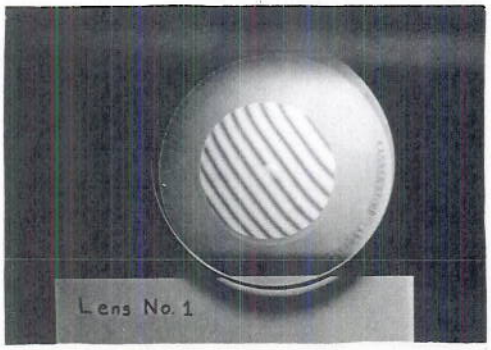


FIGURE 1

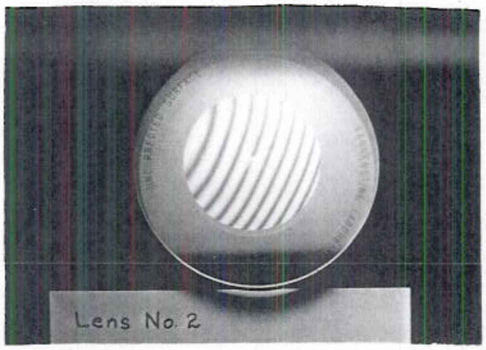


FIGURE 2

FIGURE 3

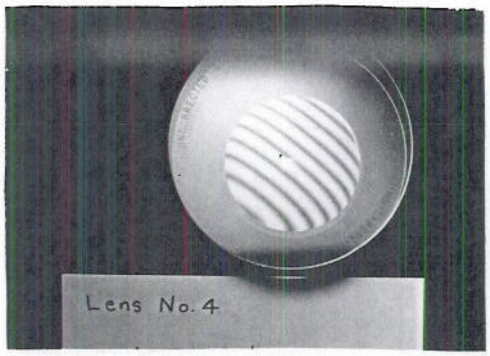


FIGURE 4

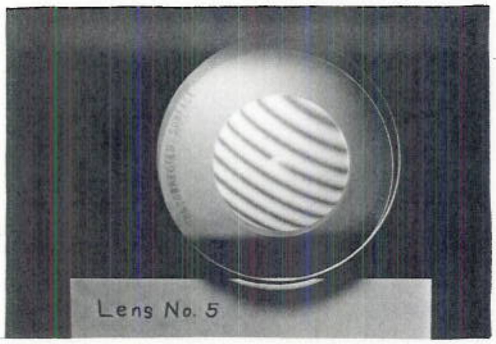


FIGURE 5

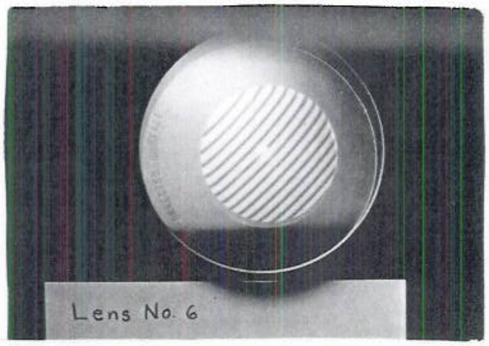


FIGURE 6

PLATE 5

CEMENTED, UNANNEALED LENSES

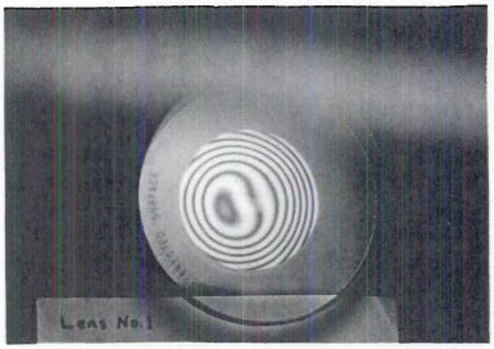


FIGURE 1

FIGURE 2

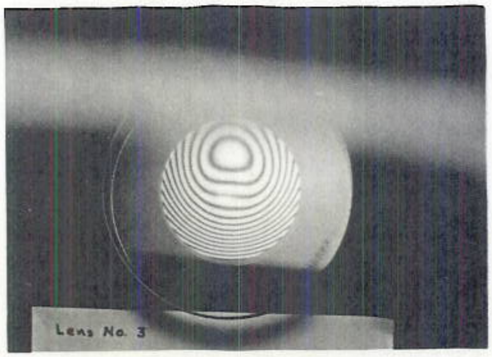


FIGURE 3

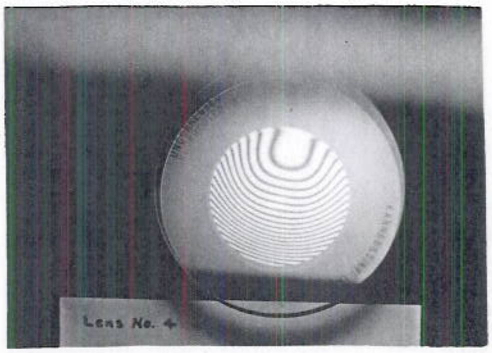


FIGURE 4

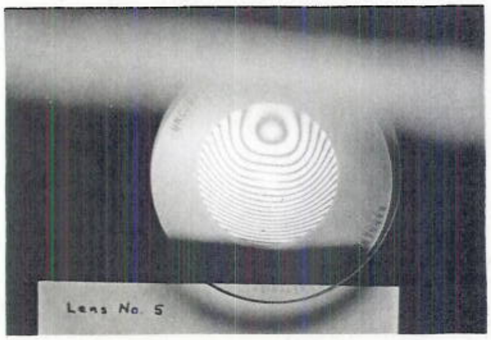


FIGURE 5

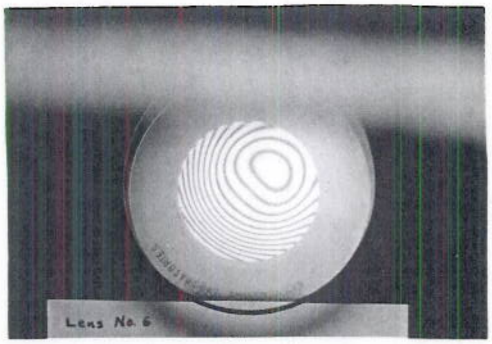


FIGURE 6

PLATE 6

CEMENTED, ANNEALED 4 HOURS

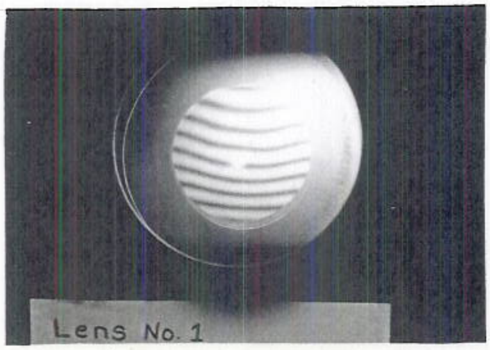


FIGURE 1

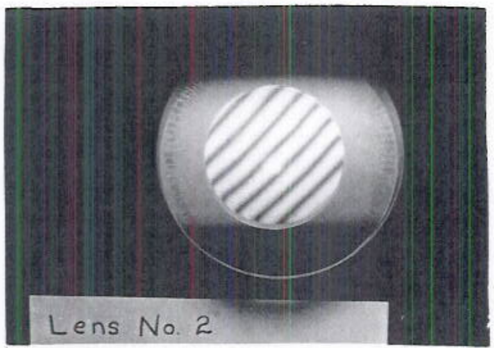


FIGURE 2

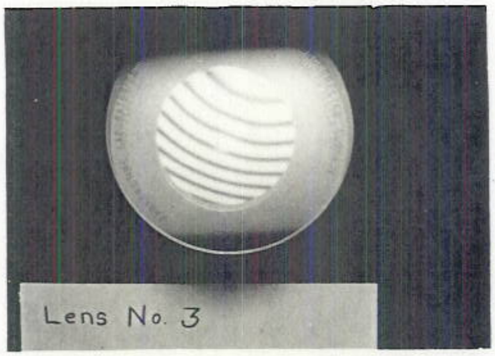
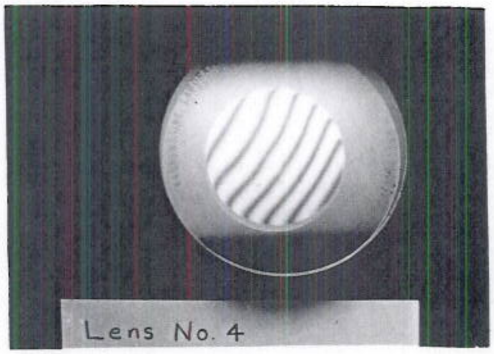


FIGURE 3



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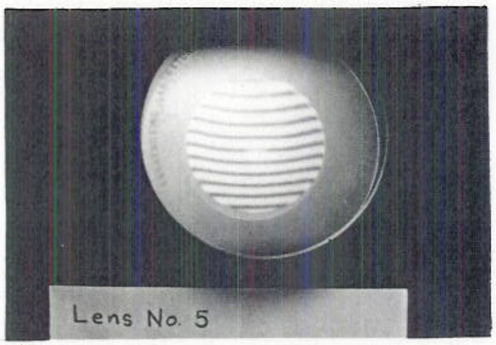

FIGURE 5

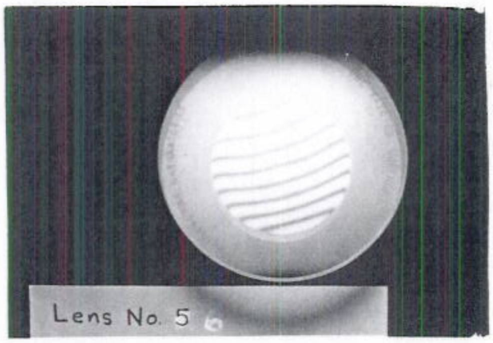

FIGURE 6

CEMENTED, ANNEALED 5 HOURS

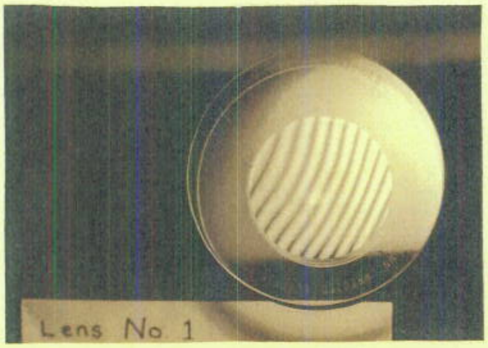

FIGURE 1

FIGURE 2

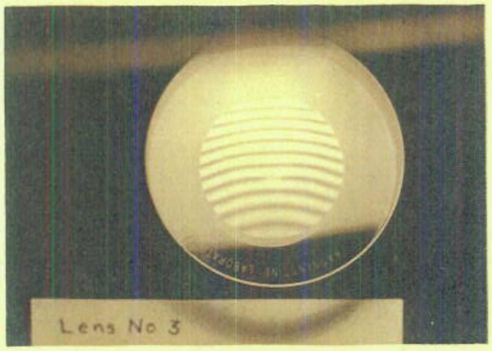

FIGURE 3

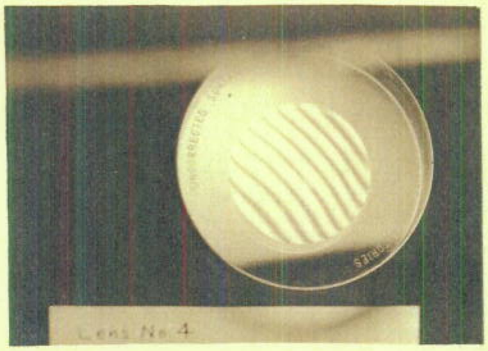

FIGURE 4

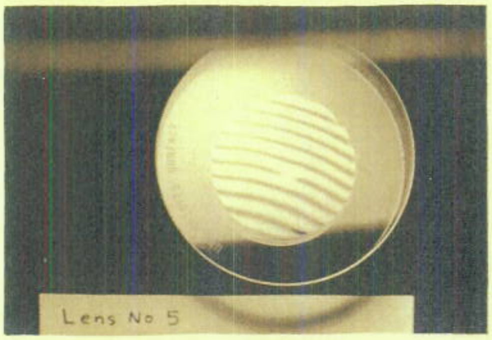

FIGURE 5

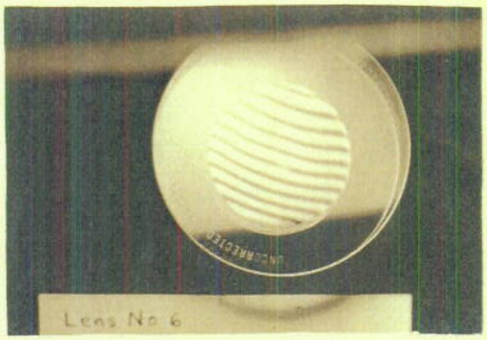

FIGURE 6

PLATE 8

DISTRIBUTION

BuOrd	(10)
ORI	(1)
BuShips	(2)
BuAer	(2)
OBS	(2)