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UNIVERSITY OF LOUISVILLE

# HEAT SEALING PROPERTIES OF ETHYL CELLULOSE MODIFIED LACQUERS

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WILLIAM B. MOORE JR.

SEPTEMBER, 1947

# HEAT SEALING PROPERTIES OF ETHYL CELLULOSE MODIFIED LACQUERS

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SEPTEMBER, 1947

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The author wishes to acknowledge
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# ABSTRACT

The heat sealing properties of lacquers containing ethylcellulose were studied. Adhesion, block, flexibility, and appearance were considered to be the properties most important in determining the usefulness of a heat sealing agent.

The experimental procedure consisted in the formulation and testing of various lacquer systems. Data from these systems are presented in the form of areas on triangular composition plots.

Two lacquers, HS 148 and HS 196, fulfilled the problem requirements. The compositions of these lacquers are

| HS 148 | | HS 196 | |
|---|---|---|---|
| ethylcellulose........... | 55.0% | ethylcellulose.......... | 45.0% |
| Dow resin 276-V2......... | 30.0 | Dow resin 276-V2........ | 40.0 |
| tricresyl phosphate...... | 14.7 | Dow plasticizer No. 5... | 14.7 |
| carnauba wax............. | 0.3 | carnauba wax............ | 0.3 |

HS 148 samples have been applied on industrial heat sealing machinery. The seals made in this manner compare favorably with those produced on the same machines with normally accepted industrial lacquers. HS 196 produces seals slightly inferior to those of HS 148. It is recommended for use in handling foods, however, as it has no detectable toxicity.

# INTRODUCTION

This investigation is a study of the bonding characteristics of films containing ethylcellulose.

Adhesives are usually classified as animal derivative, vegetable derivative, cellulose derivative, or synthetic. Animal glues, usually cold liquids, are composed of liquid extracts from the bones, skins, and hoofs of animals. Casein adhesives, made from a product of the coagulation of milk, are also classified as of animal origin. Animal glues are general purpose adhesives which produce medium strength bonds between many different materials.

The term vegetable adhesive includes gum emulsions, dextrin adhesives, latex cements, natural resin adhesives. Gum adhesives, consisting of aqueous emulsions of natural gums, such as arabic, are used for cheap, low strength bonding. Dextrin glues are prepared from a product of the degradation of starch at higher temperatures. When moisture resistance is unimportant dextrin-base adhesives form good bonds between wood, paper, and similar substances. Rubber latex is the cured milk sap of the rubber tree or quauale shrub. An extremely sticky substance, latex has found wide usage in general purpose bonding. Shellacs and rosins are used either alone or with added compounds to form many adhesives. Their use is similar to that of synthetic resins in adhesives. The principal application of natural rosins is in mixtures containing other vegetable or synthetic materials. Cellulose derivative lacquers are widely used to replace both rubber cements and animal glues. Either as pure substances or mixed with plasticizers and resins, cellulose derivatives are dissolved in suitable solvents and applied as cold liquids. Melted from solid form, cellulose derivatives are called "hot melts". The derivatives most common to coating and adhesive applications are nitro cellulose, cellulose acetate, and ethyl cellulose. Cellulose derivatives may be made to form strong water-resistant bonds. They are, however, affected by heat, organic solvents, and, in some cases, light.

Synthetic adhesives are too numerous and varied in form to be discussed individually. Synthetic compounds have been made whose properties duplicate and surpass those of many natural adhesives. A large majority of these synthetics are phenolic, urea, acrylic, or vinyl in nature. The application of synthetic adhesives is for strong, permanently resistant bonds.

Adhesives are applied in several ways. The oldest and most common consists of brushing a liquid adhesive material on one or both surfaces to be joined and holding the coated surfaces together until the liquid has dried or set. In many cases heat is applied to speed up the drying or setting operation. Although liquid application is often accomplished by machine brushes, rolls, or doctor knives, the principle remains unchanged.

The so called dry method (1) consists of coating liquid adhesives on the surfaces to be bonded. After drying the coated surface, bonding is obtained by means of heat and pressure. Both thermoplastic and thermosetting adhesives can be handled in this manner. Although several other means of applying adhesives are used, the liquid and dry principles cover the majority of present day techniques.

Industries using adhesives on a large scale are numerous and wide spread. Wood fabrication and packaging can be chosen as representative of those users. Aside from the manufacture of cheap toys, novelties, and various low strength articles, the fabrication of wood demands high strength adhesives. The manufacture of plywood furniture and prefabricated wooden parts requires durable bonds that will strengthen rather than weaken the final product. Synthetic thermosetting resin adhesives are, therefore, best suited to wood fabrication. The two adhesives most common to that industry are phenol and urea formaldehydes. Both glues of phenol and urea, like most thermosetting adhesives, must be bonded under heat and pressures. Curing requires from one second to four hours, and heated presses are many times suited to industries employing thermosetting adhesives.

The packaging industry used some form of each adhesive classified. Bonding metal foils, papers, plastics, and cardboards requires many glues and techniques. The flimsy, temporary nature of products from the packaging industry make high bond strengths unnecessary; therefore there is limited use for the high strength synthetics used for wood bonding.

Until recently, all packaging operations used liquid animal or vegetable glue. Those glues still predominate in that field. In the last fifteen years, however, the dry method of adhesive application has become more acceptable. In order to increase production speed and eliminate the handling of liquid glues, bonds are made by sealing certain thermoplastic films under heat and pressure. That process is known as heat-sealing. Adhesives or heat sealing agents are coated on the material to be bonded. The coated foil or paper can then be sealed or packed for distribution to other sealing operations.

Heat sealing agents are thermoplastic materials which require only instantaneous applications of heat and pressure for bonding. Continuous rapid sealing processes can therefore be used. The high sealing speeds and almost immediate setting of the bond after sealing makes heat sealing a process readily adapted to the packaging industry. Heated rolls, metal tapes, irons, wheels, and presses are all utilized to form heat seals.

Heat sealing films are classified by means of the constituent present in the highest concentration. Classified in that way, most heat sealing agents are either wax, rubber, resin, or cellulose derivative adhesives. Adhesives of each type almost invariably contain one of the other named constituents. Many contain all of them.

Wax coatings have been used for heat sealing more than have the other types. Paraffin coatings, beeswax films, carnauba hot melts, and other microcrystalline waxes have been sealed by means of heat for many years. The use of wax to seal letters dates back to the Roman Empire. Bonds of wax sealed coatings are, at best, of low strength. Wax seals are used predominantly for applications where moisture resistance, not strength, controls.

Rubber and resin compounds have not been widely used as heat sealing agents. Both are frequently found in heat sealing lacquers as modifying agents, but seldom are they present in amounts over 25 per cent. Rubber derivative adhesives are soft and sticky or tacky at relatively low temperatures. That property limits the use of rubber in lacquers which must be non-tacky for shipment and storage.

Properly formulated cellulose derivative lacquers offer the non-tackiness of wax at low temperatures and satisfactory adhesion at elevated temperatures. Nitrocellulose, ethylcellulose, and cellulose acetate all have thermal properties suited to the temperature and pressure requirements of heat sealing. Ethylcellulose, of the three, is recognized as the best material for heat sealing (2).

A heat sealing agent for the packaging industry must meet several specifications. The first and most important is that the material produce satisfactory bonds at the specified temperatures. In order that rolls of foil or paper coated with such a film can be stored the lacquer must not be sticky or tacky at ordinary storage temperatures. To adhere to the foils and papers used in the packaging industry the film must be flexible. It is of particular importance to the food packager that compounds used in connection with edibles be free from taste, odor, and toxicity.

The work described in the following thesis is an attempt to formulate a heat sealing agent with ethylcellulose as a major constituent. The coating was to be applied as a liquid and dried before sealing. Under minimum pressure it was to seal at temperatures from 120 to 160°C, to aluminum foil, glassene paper (3), cellophane, films of the lacquer itself, and other related substances. The film was to be tack-free after 24 hours exposure to 50°C. under one pound per square inch. It could have no taste, odor, or toxicity.

It must be flexible and suited to standard means of application.

# HISTORICAL

The use of thermoplastic waxes for the sealing of letters and private papers was, probably, the first distinct heat sealing operation (4). Seals of that type have been found among relics of ancient Egypt.

Heat sealing has not, until recently, had a separate place in the field of adhesion. The use of heat and pressure to aid drying or setting of liquid glues was, of course, a common practice; that practice, however, cannot be termed heat sealing. It is purely a means by which the liquid sealing operation is sped up and improved. Work with hot melt coatings led to the development of heat sealing agents for industrial operations. R. Gordan (5) was among the first to recognize the use of ethyl cellulose hot melt coatings and their use as adhesives. He introduced a coating containing ethylcellulose and latex to be applied in melted form. The film was quite tacky and therefore not suited to storage on rolls or in packages.

Staundinger (6) and Henkle (7,8), closely following Gordan, patented hot melt coatings in 1938 and 1939. The coatings patented by Staundinger and the two by Henkle differed but slightly. Both contained ethylcellulose, starch, and some polymer. Coatings of this type polymerize on being applied as hot melts and have no further application as heat sealing agents.

The most significant patents on hot melt and heat sealing compounds issued in 1939-1940 were to Bidald and Farre (9), Nobel (10) and C. E. Pitman (11). Those patents covered three phase formulations of ethylcellulose, resin, and plasticizer. The films of Bidald and Farre and Nobel were hot melt adhesives. That of Pitman was designed to be applied in melted form or from solvent solution. Mr. Pitman also claimed that films, when formulated according to his specifications, when placed together will seal under slight addition of heat. I. G. Farben and Company (12), also in 1914, referred to a lacquer having properties similar to those developed by Pitman. They did not, however, give any indication of the content of this material.

Six patents were issued in 1942-43 for heat sealing agents. The patent to Ryan and Watkins (13) covered the use of cellulose sheeting in the lamination of glass for shatterproof automobile windows. The glass plates and separating ethylcellulose sheeting are bonded by means of heat and pressure. A plasticizer is added to the ethylcellulose sheeting to lower its melting temperature. Both Kauppe (14) and Thinius (15) obtained patents for films to be heat sealed to tin and lead foils. Each contained ethylcellulose, phosphoric acid, and a plasticizer. W. J. Barrow (16) developed a film composed of ethylcellulose and a plasticizer to preserve old parchments. The parchments are coated by hot pressing the ethylcellulose film to the surface to be coated. Temperatures of less than 100 degrees C. are used in the process. Alexander Szware (17) a Canadian, and John M. DeBell (18), an Englishman, patented, almost simultaneously, heat sealing agents that today are widely used in the packaging industry. The two lacquers differ in both composition and plasticizer. They are, however, of the same three component type, containing ethylcellulose, pine wood rosin, and a plasticizer.

Leinbach (19), in 1943, made a substantial literary contribution to the theory and practice of heat-sealing. Mr. Leinbach discussed both heat-sealing and heat sealing agents. His major contribution was in proposing certain specifications for the standardization of the evaluation tests of heat sealing lacquers. Mr. Leinbach defined heat sealing only from the standpoint of sealing a film to films of the same material.

A paper by Binner and Miller (20), in 1944, broadened Leinbach's definition to include sealing a thermoplastic film to any other material. The paper also discussed the process of laminating foils and papers by means of heat sealing methods.

The field of patents on ethylcellulose containing heat sealing agents was very broad in 1944. Among those receiving most attention were patents to Collins (21), Koch (22), Robinson (23), Bacon (24), and Mack (25). Collins claimed an ethylcellulose film for laminating plastics suitable for use as phonograph records. The film has a high melting temperature and strong resistance to cold flow. Koch, Robinson, Bacon, and Mack all patented three component ethylcellulose heat sealing lacquers. Each of those agents was designed for the bonding of packaging papers.

The year 1945 produced only two heat sealing agents containing ethylcellulose. In the first, Rhodes and Wendorf (26) perfected an ethylcellulose wax combination for use in paper sealing processes. The object of this combination is to produce heat sealed bonds with the water resistance of wax seals and the strength of ethyl cellulose. A form of waxed paper has been developed with this lacquer. The insolubility of the wax constituent makes it necessary to coat Rhodes and Wendorf's film as a hot melt. The second patent, awarded to N. E. Tillotson (27), covered an ethylcellulose, resin hot melt for use on papers and plastic sheeting.

The pertinent literature in 1945 was devoted, almost entirely, to discussing the heat sealing of solid plastic objects. Jones (28), Thomas (29), and Metzler (30) wrote related articles on the subject of welding plastic bodies together, the reaction to solvent sealing, heat sealing, and combinations of the two were discussed. The conclusions concerning ethylcellulose showed it to be the cellulose derivative plastic most adapted to heat sealing.

The established theories and methods for the use of ethylcellulose heat sealing lacquers were discussed in three articles published in 1946. Lamination by use of thermoplastic films and heated rolls was outlined and analysed by Smith (31) and Leinbach (32). Both the method of applying the adhesive as a liquid and the use of a solid film of adhesive were outlined and explained. A. Jones (33) compared ethyl cellulose heat sealing films to those of other cellulose esters. His conclusions recommend the use of ethylcellulose for most heat sealing operations.

# THEORY

Heat sealing, for the purpose of this discussion, will be defined as that process in which a dry thermoplastic substance is bonded to any material by means of heat.

This process consists of three operations. In proper order these operations are melting, or extreme softening in the film at the proper temperature, establishing close contact between the surfaces to be bonded, and the setting of the melt to form the bond. All these operations take place more or less instantaneously in that it is difficult to distinguish one from the other. The melting or softening of the film is brought about by contact with some outside source of heat. Varied sources are in use, including electrically heated irons, rolls, metal tapes, presses, and steam heated rolls. Recently dielectric heating has been applied in certain cases. The actual temperature to which a film is subjected is a function of the temperature of the heat source, time of exposure to the heat source, and the overall heat transfer coefficient from the source to the film. The temperature at which a film melts or becomes plastic is a function of its composition and differs for each lacquer. Pressure is applied to the softened film to establish contact between the materials to be bonded. In cases where the sealing film is only softened by the application of heat, more pressure is required to insure a good seal. Heat sealing operations are generally continuous, and both the exposure to heat and application of pressure are only momentary for each seal. Since the papers and foils are thin and retain very little heat the softened films resolidify quickly. To decrease the setting times, some operations include chilling seals immediately following the application of heat. In many instances chilling has a hardening effect which tends to strengthen the bond.

Heat sealing agents are defined as thermoplastic materials which can be formed into films or can be coated upon paper or other films and are reasonably normal, nonsticky solids at ordinary temperatures, but which melt or become very sticky at temperatures ranging from 150 to 300 degrees F. (34).

As in the case of paraffin wax, some of these agents are pure substances. The large majority, however, are produced from the combination of two or more pure constituents to form a lacquer or hot melt coating. The formulation of a coating to be used in heat sealing consists of adjusting three properties of the lacquer system in question. The first property to be adjusted is adhesion. The lacquer must be made to stick to the materials to be bonded. Secondly, the lacquer's melting or softening point must be adjusted to the desired temperature. The final adjustment comes in making the film as flexible as possible without softening it to the point of tackiness. In the pure state, ethylcellulose films adhere poorly to most substances. To improve adhesion the addition of certain modifying agents is necessary. The modifying agents usually added for the purpose of increasing adhesion are resins, either natural or synthetic. Resin addition, as will be discussed later, also affects other properties. Resins added to ethylcellulose films must be of a type that will form solid solutions with the ethylcellulose. By adding the proper resin, ethylcellulose films can be made to adhere to almost any surface. Ethylcellulose, in the pure state has a melting temperature of from 170 to 220 degrees C. Its exact melting point is a function of its ethoxy content. The ethoxy content is a measure of the number of $C_2H_5$ units joined to each cellulose ring. Figure 1 is a curve correlating melting temperature with ethoxy content of pure ethylcellulose.

To change the temperature of pure ethylcellulose, it is necessary to add materials to different melting points. In addition to resins, non drying liquids called "plasticizers" are added for the purpose of melting point control. For general heat sealing the melting point of pure ethylcellulose is too high. It is the general rule, therefore, that the modifying resin and plasticizer have melting points below that of ethylcellulose. The resins most common to coating applications melt at temperatures of from 0 degrees C. to 150 degrees C.

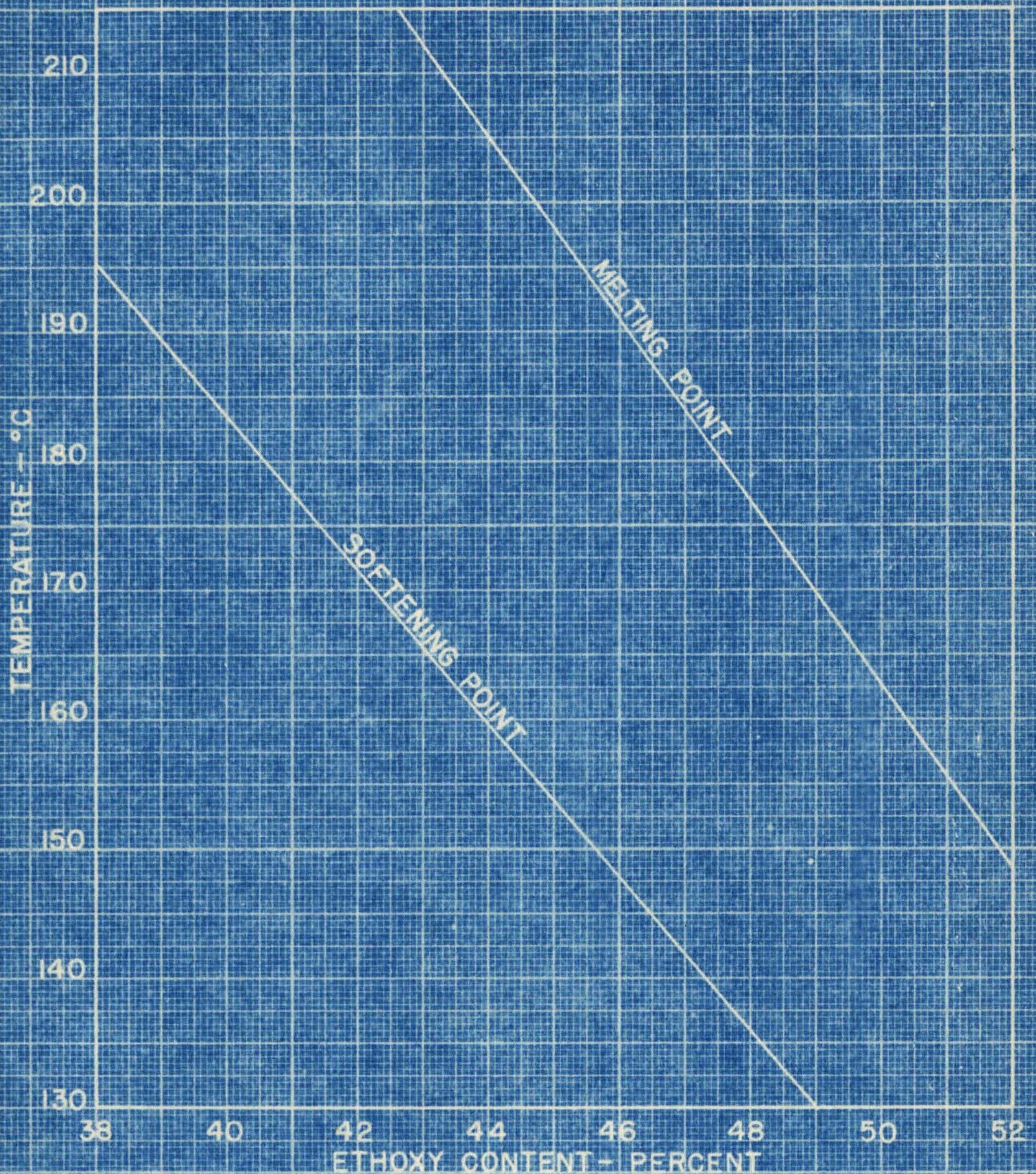


Figure 1

THE EFFECT OF ETHOXY CONTENT ON THE MELTING POINT OF FILMS OF PURE ETHYL CELLULOSE

There are resins designed for extremes in temperature, but they are not widely used as lacquer constituents. Plasticizers which are liquids at normal temperatures melt at temperatures below 0°C. The addition of either or both of these materials, if a solid solution with ethylcellulose is formed, results in a temperature below that of ethylcellulose. Figure 2 is the melting point diagram for ethylcellulose of 45% ethoxy content, in solid solution with Amberol F-7.

The term compatibility is used to designate the composition range over which two or more constituents go together to form a homogenous solid solution. The addition to a system of enough of any one component to exceed the limit of compatibility gives a film having a non-homogenous appearance. Such an appearance is called blushing. By proper addition of resins and plasticizers compatible with ehtylcellulose and having known thermal properties, a film can be made having the desired melting point.

Films of ethyl cellulose are quite flexible. The addition, however, of solid resins tends to destroy that flexibility and form films that are too brittle for use. If such a resin is to be used, the film must be plasticized to retain flexibility. The usefulness of plasticizers is limited by their softening effect on ethyl cellulose films. Films only slightly softer than pure ethyl cellulose begin to show

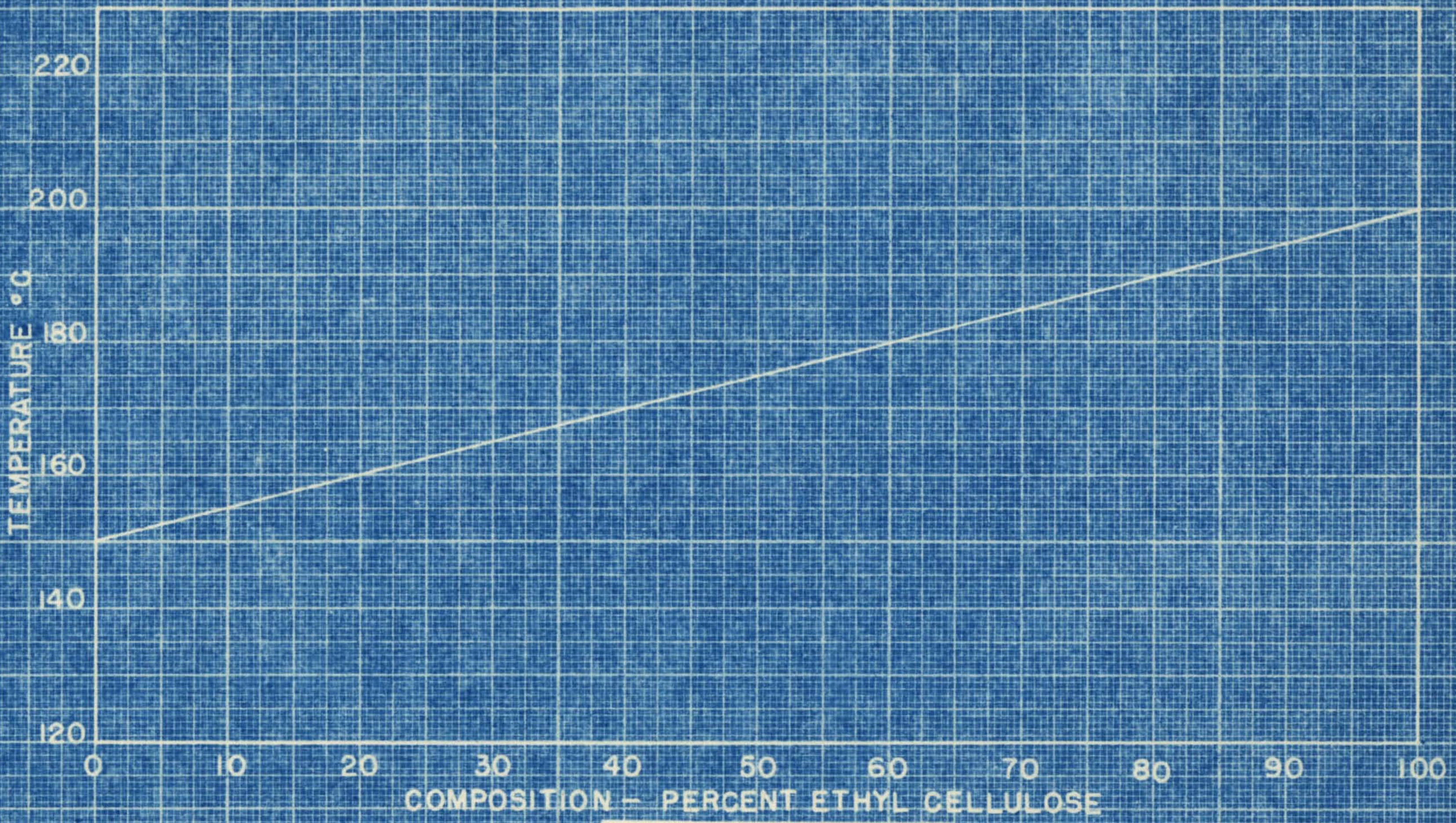


Figure 2

MELTING POINT DIAGRAM FOR THE SYSTEM ETHYL CELLULOSE-AMBEROL F7 signs of blocking under normal storage conditions of heat and pressure.

The adjustment of adhesion, melting temperature, flexibility, and blocking characteristics is a matter of experimental formulation. In practice, known mixtures of ethyl cellulose, resin, and plasticizer are dissolved in some suitable organic solvent. The liquids thus formed are coated on some carrier medium and evaluation tests made. The general requirement of resins and plasticizers is that they increase adhesion, lower the melting point from that of ethylcellulose, preserve the film flexibility, and have minimum softening effect.

Ethyl cellulose lacquer systems, as has been previously explained, are three component systems. It is, therefore, convenient to express the results of property evaluations on triangular coordinate graphs (35). Such a graph is illustrated in Figure 3. It consists of an equilateral triangle divided by equally spaced lines parallel to the three bases. Each apex of the triangle represents 100% of the material there shown. Each base line represents 0% of the material shown at the opposite apex. The altitude drawn from any one apex is divided into 100 equidistant units representing per cents from 1 to 100.

The perpendicular distances from any point on the

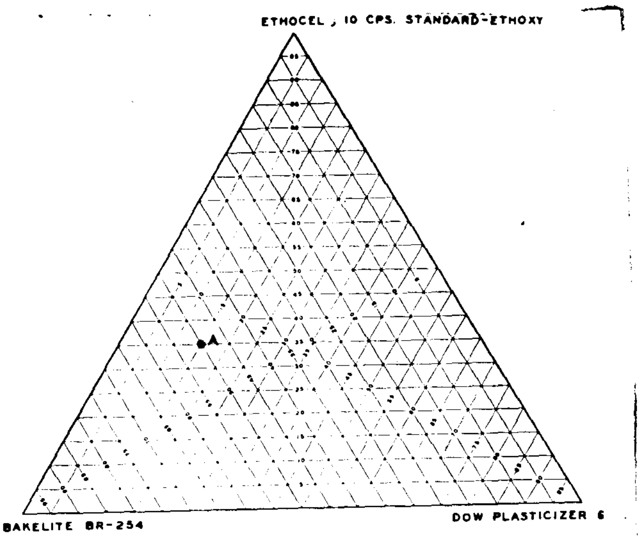


Figure 3

PLOTTING A LACQUER COMPOSITION
ON A THREE COMPONENT DIAGRAM

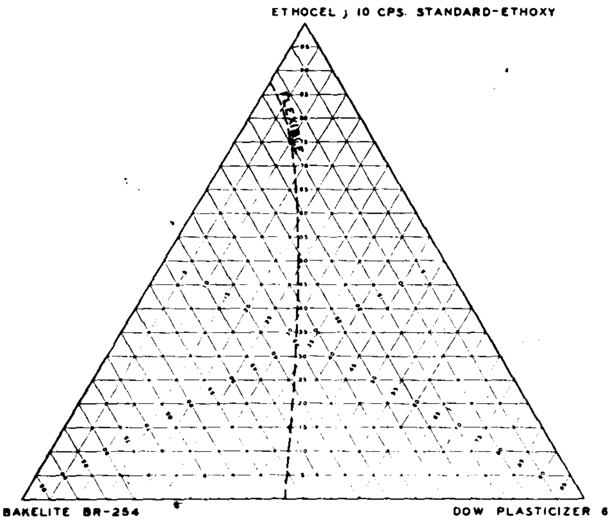


Figure 4

DEFINING THE AREA OF LACQUER
COMPOSITIONS WHICH PASS THE
FLEXIBILITY TEST

surface of the diagram to the three sides is equal to the altitude of the triangle. Therefore, any point within the triangle represents 100 parts of total solids. For example, point A represents a lacquer containing 50% Bakelite BR-254, 35% Ethyl cellulose, and 15% Dow Plasticizer 6, or a total of 100%. It is evident, therefore, that all possible mixtures of the three components are represented on one trilinear diagram.

Lacquers are formulated to represent points evenly distributed over their triangular coordinate diagram (36). The lacquers thus formulated are tested for the properties described previously. By connecting with a continuous line all compositions having the same property, a curve is obtained. That curve separates areas passing the tests from those that do not. Figure 5 is a curve of the type described above. Figures 5 and 6 are similar diagrams showing cold check resistance and print resistance. Customarily, the area containing the descriptive word has that property designated by the word.

A system, to satisfy the requirements specified for this work, must have a triangular chart whose flexibility, non-blocking, and adhesive areas overlap each other.

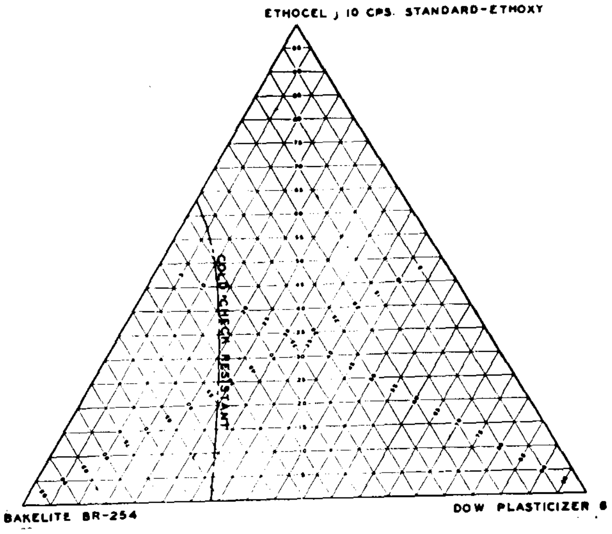


Figure 5

DEFINING THE AREA OF LACQUER COMPOSITIONS WHICH HAVE COLD CHECK RESISTANCE

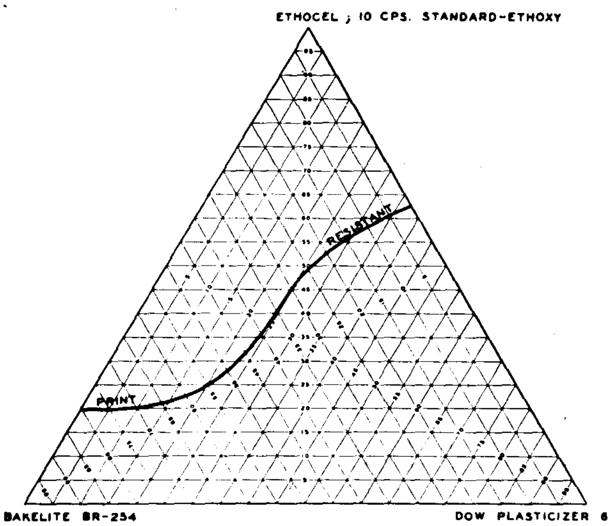


Figure 6

DEFINING THE AREA OF LACQUER COMPOSITIONS WHICH ARE PRINT RESISTANT

# EXPERIMENTAL

## PROCEDURE

The experimental procedure followed consisted of evaluating the heat sealing properties of different lacquer systems. The evaluation was made up of three operations: formulation, application, and testing.

Triangular composition diagrams were prepared for each system to be tested. On these diagrams evenly distributed points were chosen over the entire area. The points chosen for each system are plotted on Figure 11. Each of the chosen points represented a sample lacquer formulation. Ten grams was chosen as the total solids weight for each sample. This weight made it possible to formulate, without further computation, a lacquer from compositions shown on the system's triangular chart. Samples having the desired composition were dissolved in a 70-30% mixture of toluene with ethanol. Enough solvent was added to lower the lacquer viscosity to a point where it flowed easily under the blade of a .006 inch doctor knife. Normally the amount of solvent was 7.3 cc solvent per gm. ethyl cellulose. Formulae containing carnauba wax required heat to dissolve the solids completely. An electric hot plate was used to supply the necessary heat.

Aluminum foil was specified as the medium on which test films were to be cast. The foil used on these tests was Reynolds' 2SH 2-C, .004 inches thick. Films were cast by hand on the polished face of the foil by doctor blades (37) or the Dow Ethocel Caster. Figure 7 shows films being cast with the Ethocel Caster. Both blades and caster were set to cast films to a wet thickness of .006 inches. Dry film thicknesses, determined on a Randall-Stickney thickness gauge, differed for each formulation. Films were air dried for 24 hours before testing.

The following tests were set up for the evaluation of film properties:

### Adhesion

Aluminum foil, coated with the film to be tested was cut into strips 2 by 4 inches. Strips having the same dimensions were prepared from the material to which a seal was to be made. This material was usually foil, glassine paper, cellophane, or a similar strip of coated foil. The two materials were then placed face to face, separated by the lacquer film coated on the aluminum foil strip. The two materials were sealed by pressing with an electric hand iron. The face of the iron was regulated to 150 degrees C. by means of an iron-constantan thermocouple. One pass of the iron was used. Pressure on the sample was that of the iron only and was approximately .3 psi. Sealed samples were quickly cooled to room temperature by being held on a water cooled steel plate.

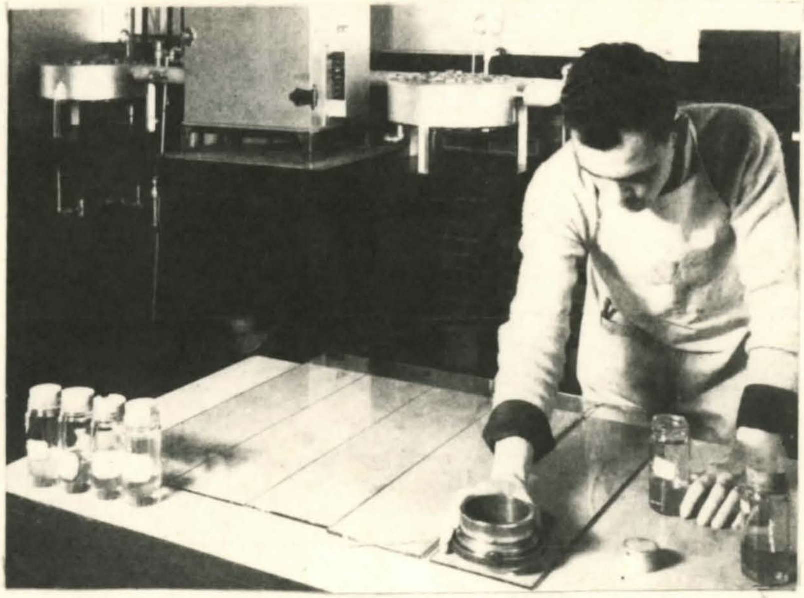


Figure 7

CASTING FILMS OF ETHYL CELLULOSE

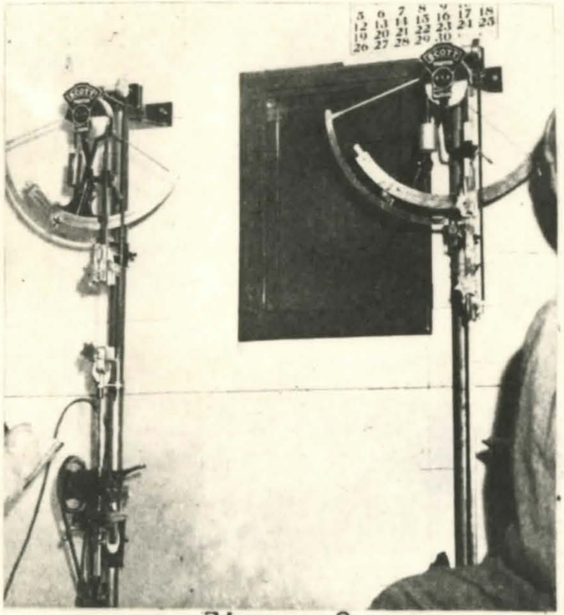


Figure 8

TESTING ETHYL CELLULOSE
FILMS ON THE SCOTT FILM
TESTER

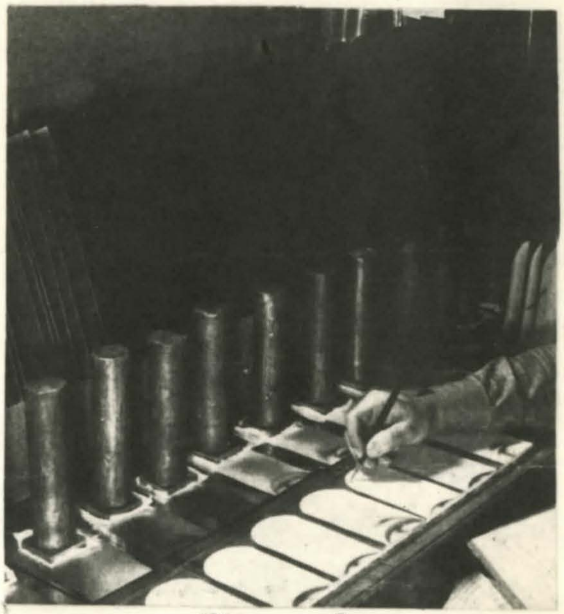


Figure 9

TESTING ETHYL CELLULOSE
FILMS BY THE PENCIL TEST

Samples, after having been sealed, were tested for adhesion. Two methods were used to make the adhesion test. The first consisted of pulling the sealed strips apart by hand. Bonds that held until the foil or paper tore were rated adhesive. Although the hand stripping method has the advantage of speed, it is not accurate. Bonds not strong enough to be tearing bonds can not be further rated by hand stripping.

Slower but more accurate adhesion tests were made on the Scott Film Tester. This method was applied to samples that sealed with strengths less than tearing bonds. The Scott Film Tester was originally designed to test tensile strengths of films, fibers, and packaging materials. It consists of a low speed, variable drive motor, a balance dial, and clamps for holding thin films. The ends of the film to be tested are placed in the two clamps. Tension is slowly applied to the film by the motor. A continuous measurement of this slowly increasing tension is registered on the scale.

Seal strengths are measured on the Scott Tester by placing the ends of the sealed materials into the clamps. Tension is then applied at right angles to the seal. Since the scale is arranged to read maximum strengths, it will show the highest strength developed by the seal before failure. Figure 8 shows Scott Film Testers in operation.

## Blocking

The problem required the film to be non-blocking at $50^{\circ}C.$ under 1 psi. Test samples for the block test, as in the adhesion test, were aluminum foil strips coated with the film to be tested. The sample strips were folded, film inside, thus making a film-to-film contact. Samples folded in that way were, then, placed on the center tray of a convection oven set at $50^{\circ}C.$ under a pressure of one psi. After 24 hours at $50^{\circ}C.$ the samples were removed from the oven and cooled to room temperature. The folded foil was then hand stripped in the same manner as were the samples tested for adhesion. Samples showing no tendency whatsoever to stick or become tacky were rated non-blocking.

## Flexibility

The flexibility of sample films was rated by hand creasing. Aluminum foil strips coated with the film to be tested were creased, film side out, by hand. The creasing was repeated with a rolling motion for 25 complete creasings. Microscopic examination revealed any film cracking caused by this test. Films showing no cracks after 25 creasings were rated as flexible.

## Compatibility

A slight haze, called blushing, is a good indication of basic incompatibility. Several other factors, however, can temporarily cause a film to blush. Improper solvent, abrupt cooling, and insufficient mixing are the most prevalent of those factors. Samples showing any tendency to blush when drying on aluminum foil were remelted. This was done by passing the coated foil over a hot plate at 200°C. Films blushing after this treatment were rated incompatible.

### Hardness

The standard Pencil Test (38) was used to rate the hardness of sample films. A set of sharpened drawing pencils was used in the test. Sample lacquers were coated on glass panels and air dried for 24 hours. Testing the films consisted of marking the films with pencils of increasing hardness. Hand pressure must be kept constant. The hardness rating of any film is reported as the softest pencil that will make a distinct mark in the film. Figure 9 shows films being subjected to the pencil test. It was decided, however, that the blocking test and hardness tests for purposes of this work duplicated each other. The hardness test was discontinued as the blocking was the more pertinent property.

### Aging

The retention of properties in films passing all other tests was checked. Foil coated with the film to be tested was cut into strips. Various forms of the coated foil, both sealed and unsealed, were made up and stored at room temperature. Adhesion, blocking, and flexibility tests were run on these samples at intervals of 7 days. Changes in the original properties of the sample were noted.

### Cold Storage

Samples passing adhesion, blocking, and flexibility tests were tested for loss of properties at cold storage temperatures (39). Samples prepared in the same way as were those for aging tests were placed in direct contact with dry ice. After 24 hours contact with dry ice, they were transferred to the freezing compartment of an 8 cu. ft. electric refrigerator. Following 72 hours in the freezing compartment, the samples were tested for adhesion, blocking, and flexibility. Changes from the original properties of the sample tested were recorded.

### Machine Tests

Samples considered to be suitable for use as heat sealing agents were tested by industrial application. Two operations in the Brown and Williamson Tobacco Company plant in Louisville, Kentucky, require a heat seal. The first consists of sealing the longitudinal paper seam on a cigarette. In the case of one particular brand a cork tipping is also sealed in this operation. A liquid glue is used to seal the cork to the cigarette paper. The overlapping cork to cork joint is the only portion of cork exposed to a sealing iron. The second operation consists of the manufacturing of a one piece cigarette package. This package, made of foil precoated with a heat sealing agent, is sealed entirely by heat sealing procedures. Figure 10 is a sample of foil laminate used in this operation. Careful inspection will show the adhesive patterns coated on the edges of the laminate. Ethyl cellulose lacquers were tested on these machines by hand coating them on rolls of cork tipping and packaging foil. The film was thoroughly dried before rerolling the foil or tipping. Cigarettes and packages were made with these coated materials. The lacquers were rated by comparing products sealed with them to those sealed by the regularly employed adhesives. The results from each system were plotted on a triangular diagram. Figures 11, 12, 13, and 14 illustrate, for the system ethyl cellulose-Nevillac S-Arochlor 1262, the method by which all the triangular diagrams were made. The diagrams were first plotted from the results of individual tests. These plots were made, as is illustrated in Figures 11, 12, and 13, by separating the lacquers passing a given test from those failing to pass the same test. The individual plots were then combined to form the overall diagram. Such a combination is illustrated in the combining of Figures 11, 12, and 13 to form Figure 14.

Figure 10

FOIL LAMINATE USED IN BROWN-WILLIAMSON

HEAT SEALING PACKAGER

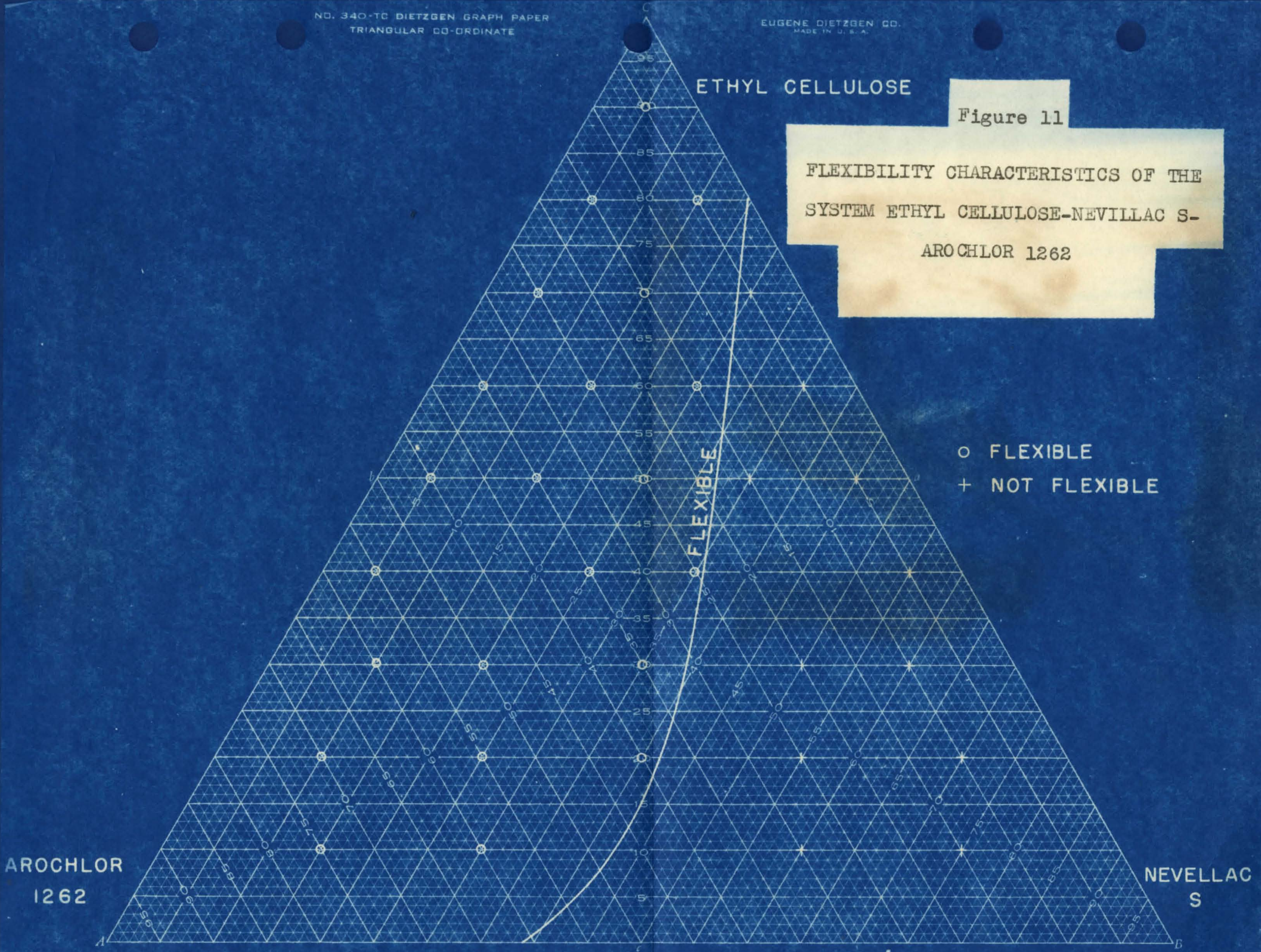


Figure 11

FLEXIBILITY CHARACTERISTICS OF THE SYSTEM ETHYL CELLULOSE-NEVILLAC S-AROCHLOR 1262

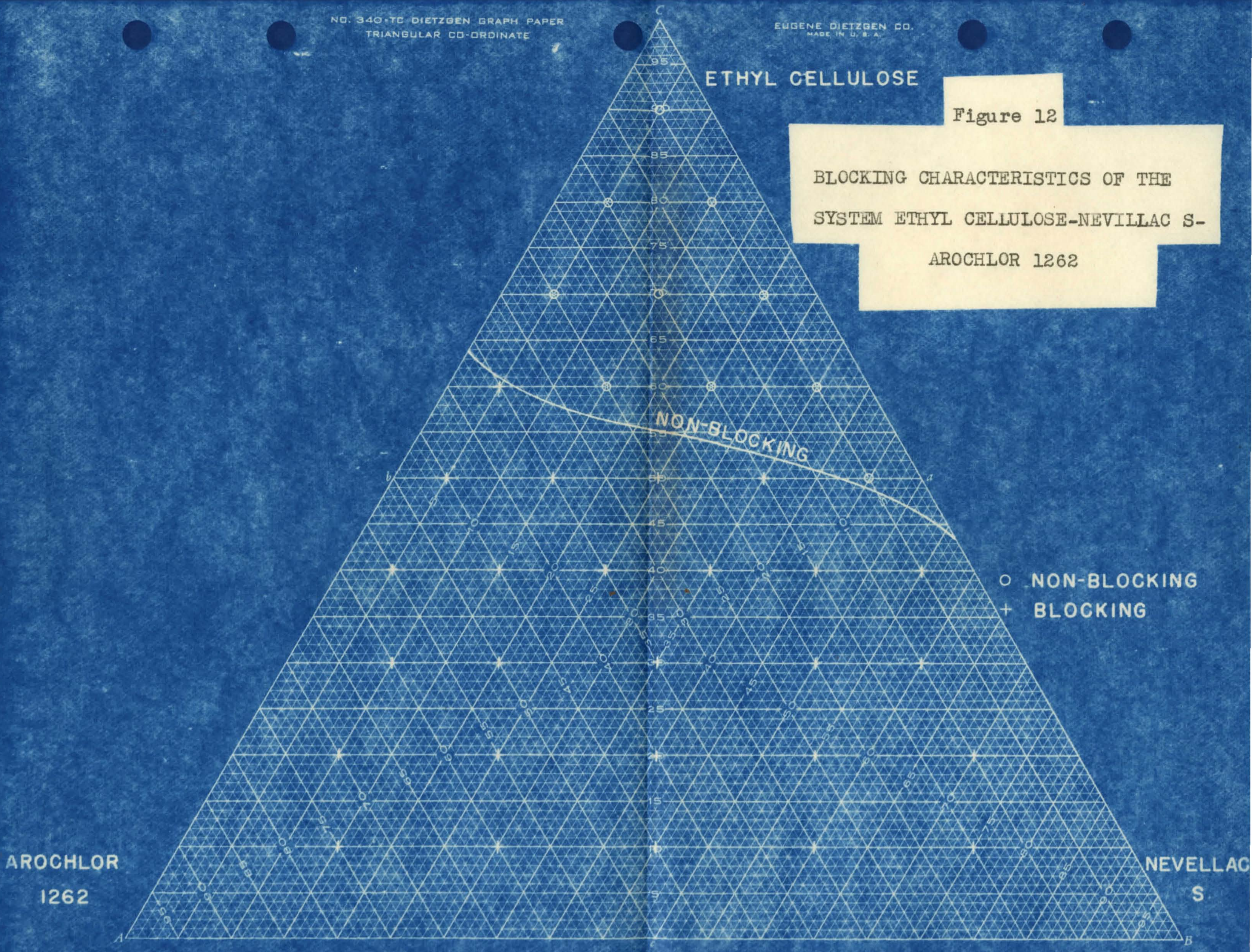


Figure 12

BLOCKING CHARACTERISTICS OF THE SYSTEM ETHYL CELLULOSE-NEVILLAC S-AROCHLOR 1262

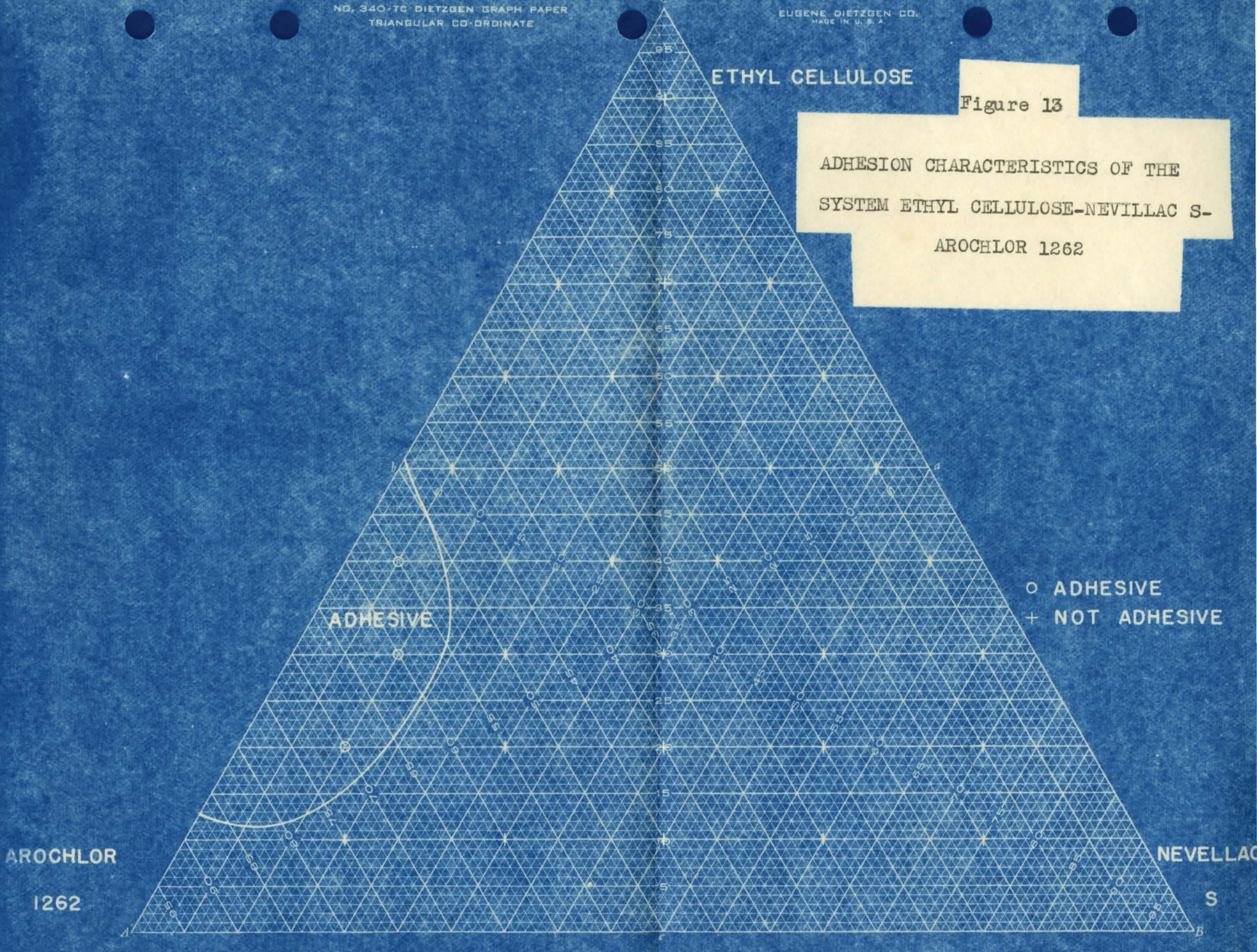


Figure 13

ADHESION CHARACTERISTICS OF THE SYSTEM ETHYL CELLULOSE-NEVILLAC S-AROCHLOR 1262

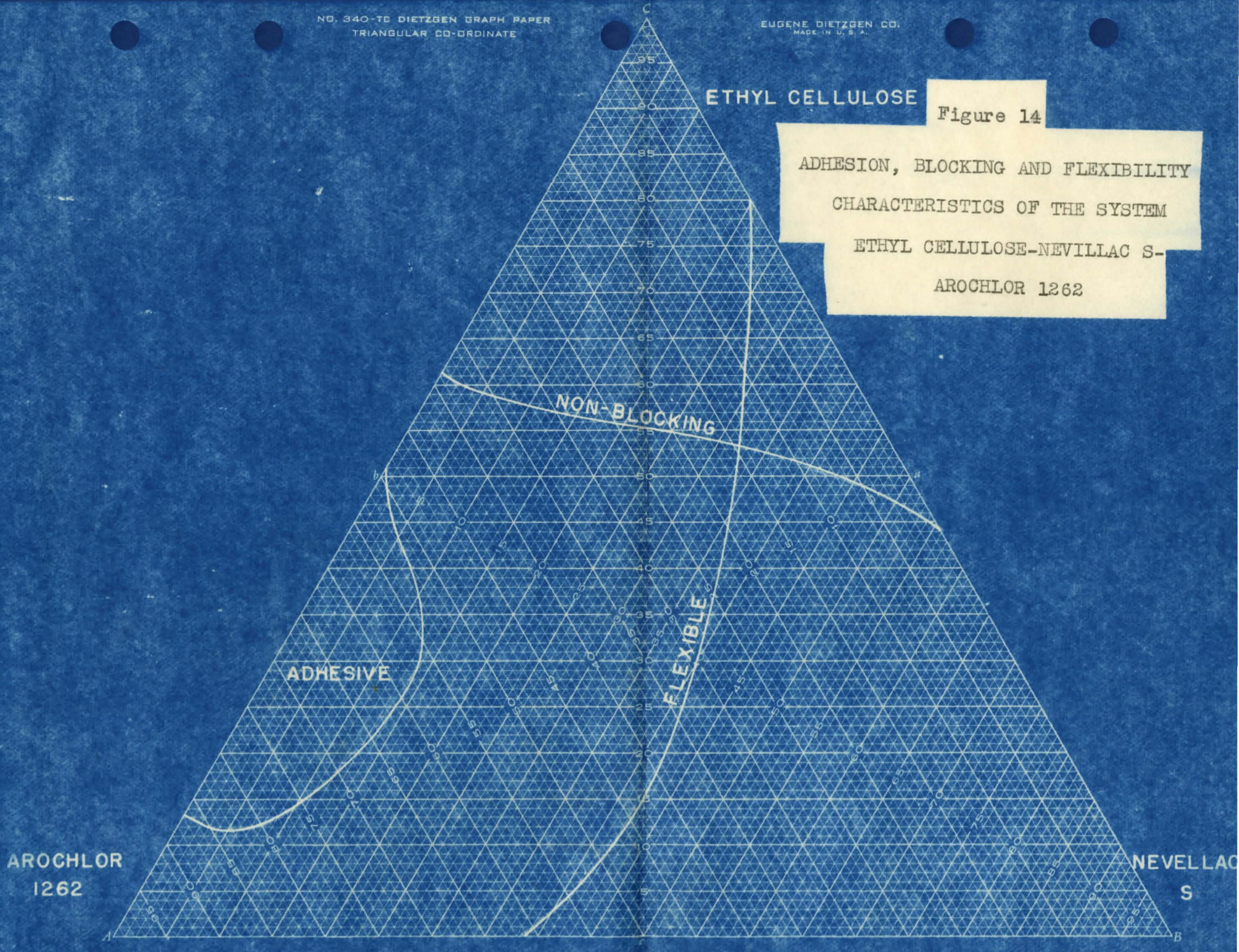


Figure 14

ADHESION, BLOCKING AND FLEXIBILITY CHARACTERISTICS OF THE SYSTEM ETHYL CELLULOSE-NEVILLAC S-AROCHLOR 1262

## RESULTS

Results from adhesion, blocking, and flexibility tests were rated as good, fair, and poor. "Good" indicates satisfactory passage of the test. "Fair" represents intermediate results while "poor" indicates complete failure of the test.

A large majority of the systems tested were not suitable for the formulation of a heat sealing lacquer. In general the best adhesive properties occurred in lacquers of high resin and low ethyl cellulose composition. High ethyl cellulose compositions give the best blocking characteristics. Only three systems were found from which lacquers combining adhesion and non-block could be formulated. Table I indicates the results obtained by rating, for each system tested, the properties of the lacquer that best combined the properties adhesion, non-block, and flexibility. Tables II, III, and IV list the properties of all two-component lacquers tested. Properties of all three-component lacquers are graphically shown in Figures 14 through 21.

The three systems best combining these properties are ethyl cellulose-Arochlor 1262, ethyl cellulose-Dow resin 276-V2-tricresyl phosphate, and ethyl cellulose-Dow resin 276-V2-Dow plasticizer No. 5. Carnauba wax was added, in small quantities, to each of these systems to improve blocking

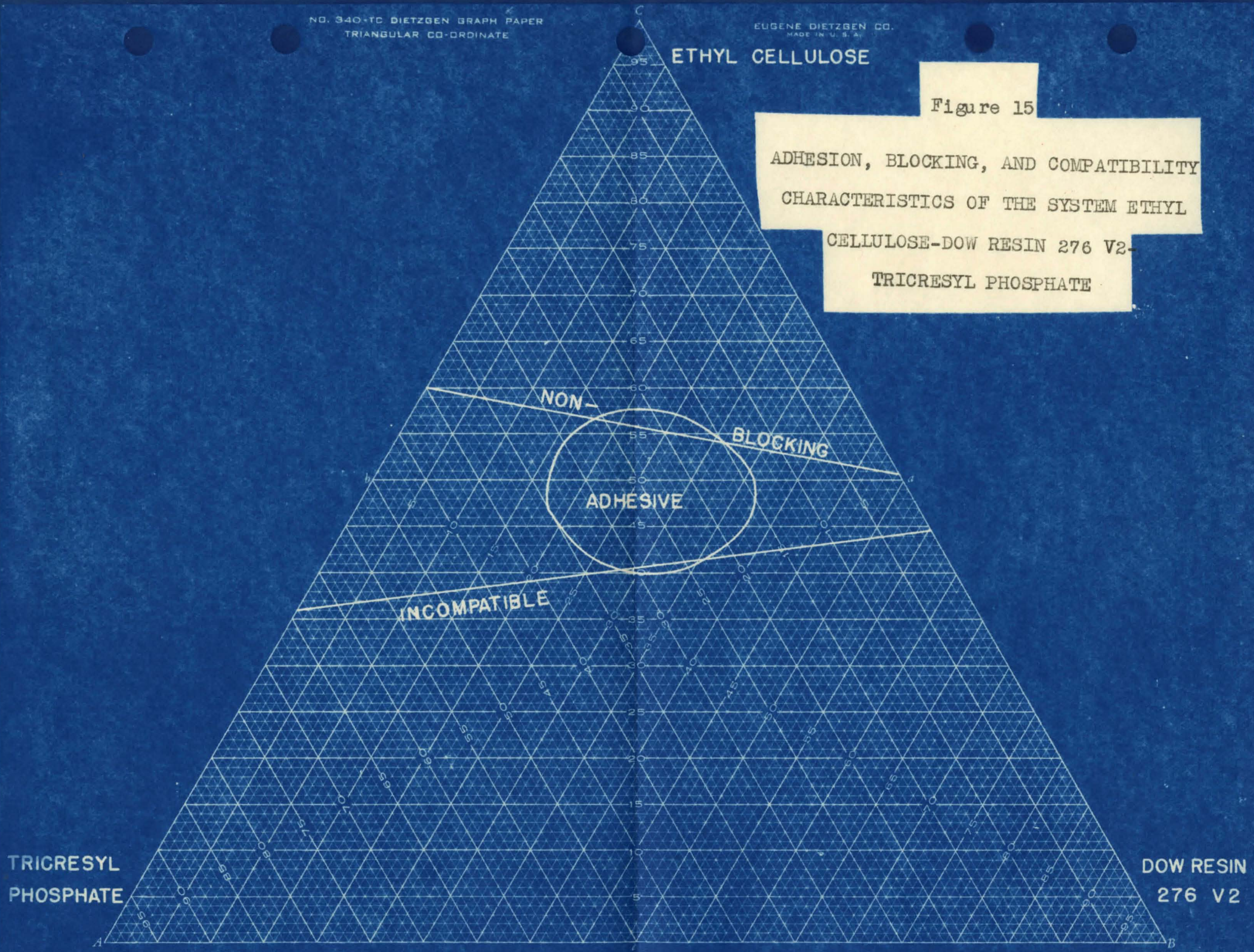


Figure 15

ADHESION, BLOCKING, AND COMPATIBILITY CHARACTERISTICS OF THE SYSTEM ETHYL CELLULOSE-DOW RESIN 276 V2-TRICRESYL PHOSPHATE

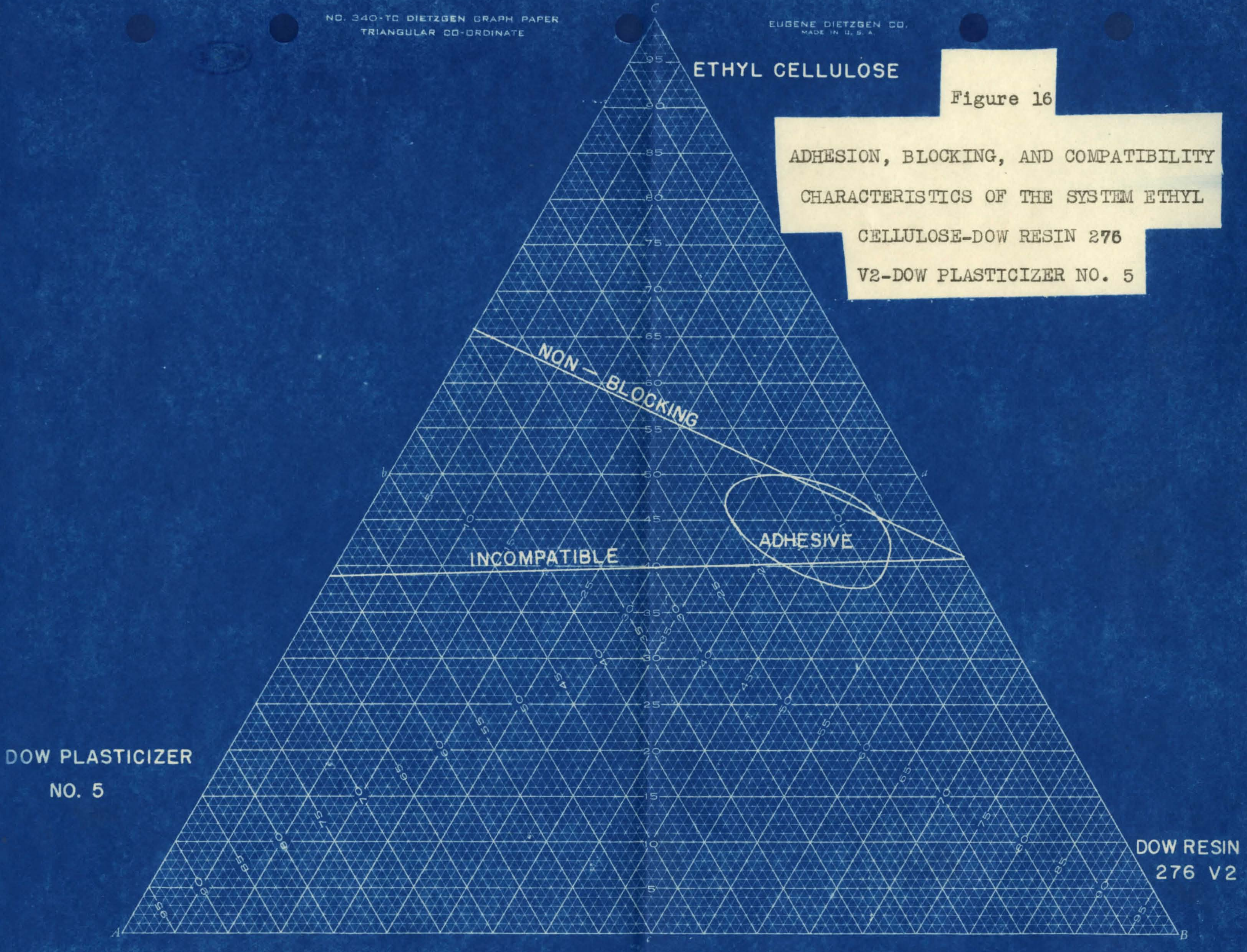


Figure 16

ADHESION, BLOCKING, AND COMPATIBILITY CHARACTERISTICS OF THE SYSTEM ETHYL CELLULOSE-DOW RESIN 276 V2-DOW PLASTICIZER NO. 5

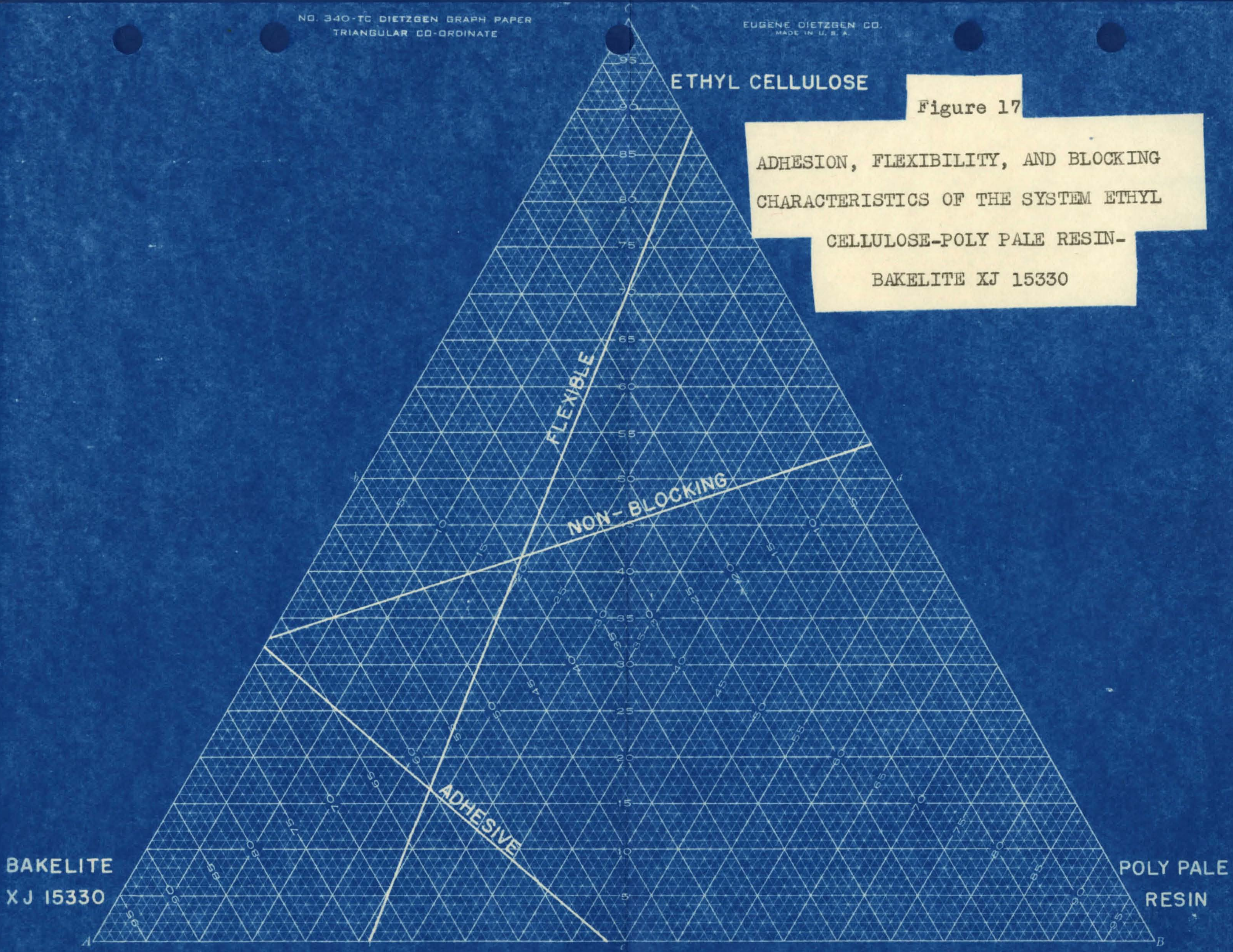
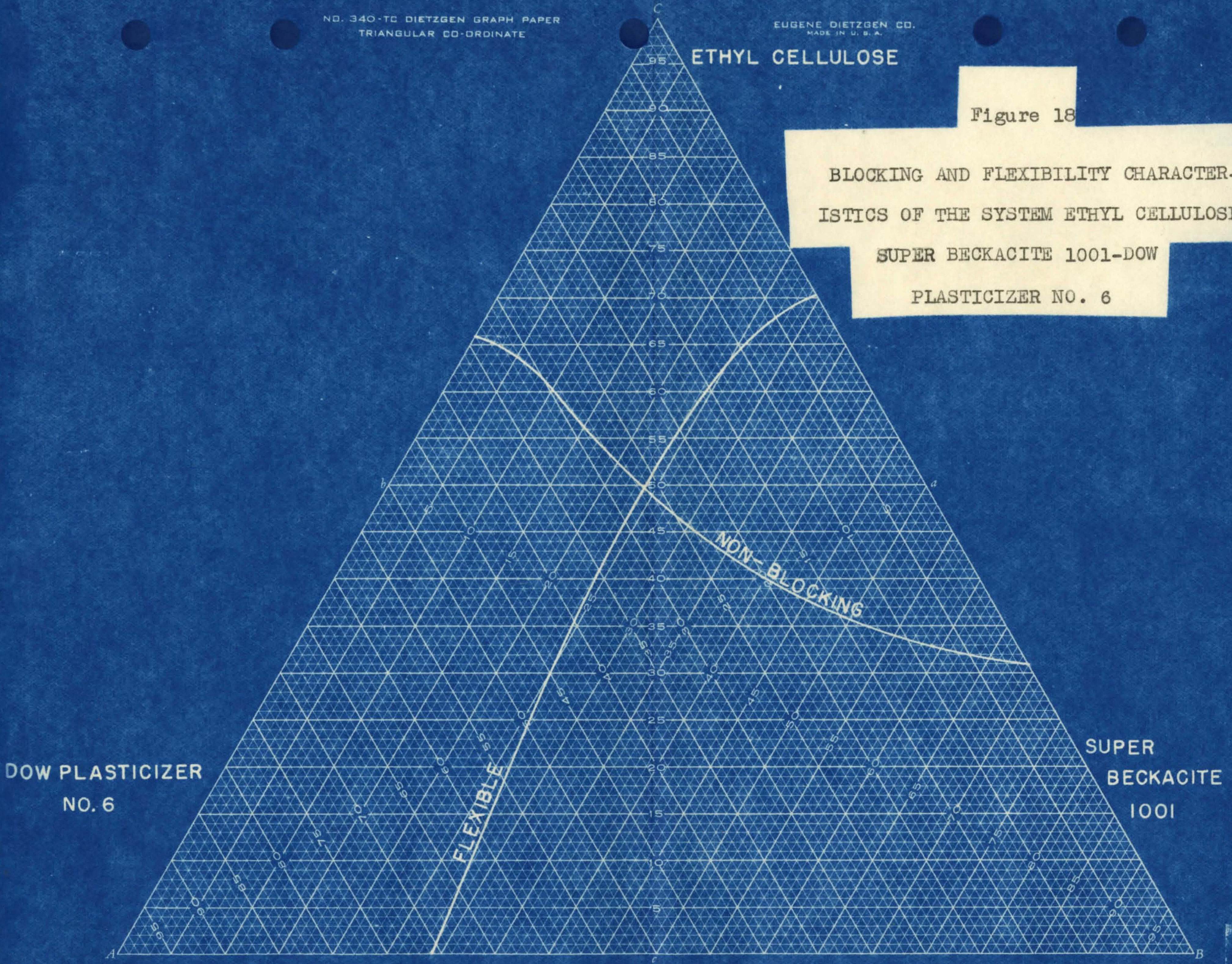


Figure 17

ADHESION, FLEXIBILITY, AND BLOCKING CHARACTERISTICS OF THE SYSTEM ETHYL CELLULOSE-POLY PALE RESIN-BAKELITE XJ 15330

Figure 18

BLOCKING AND FLEXIBILITY CHARACTERISTICS OF THE SYSTEM ETHYL CELLULOSE-SUPER BECKACITE 1001-DOW PLASTICIZER NO. 6



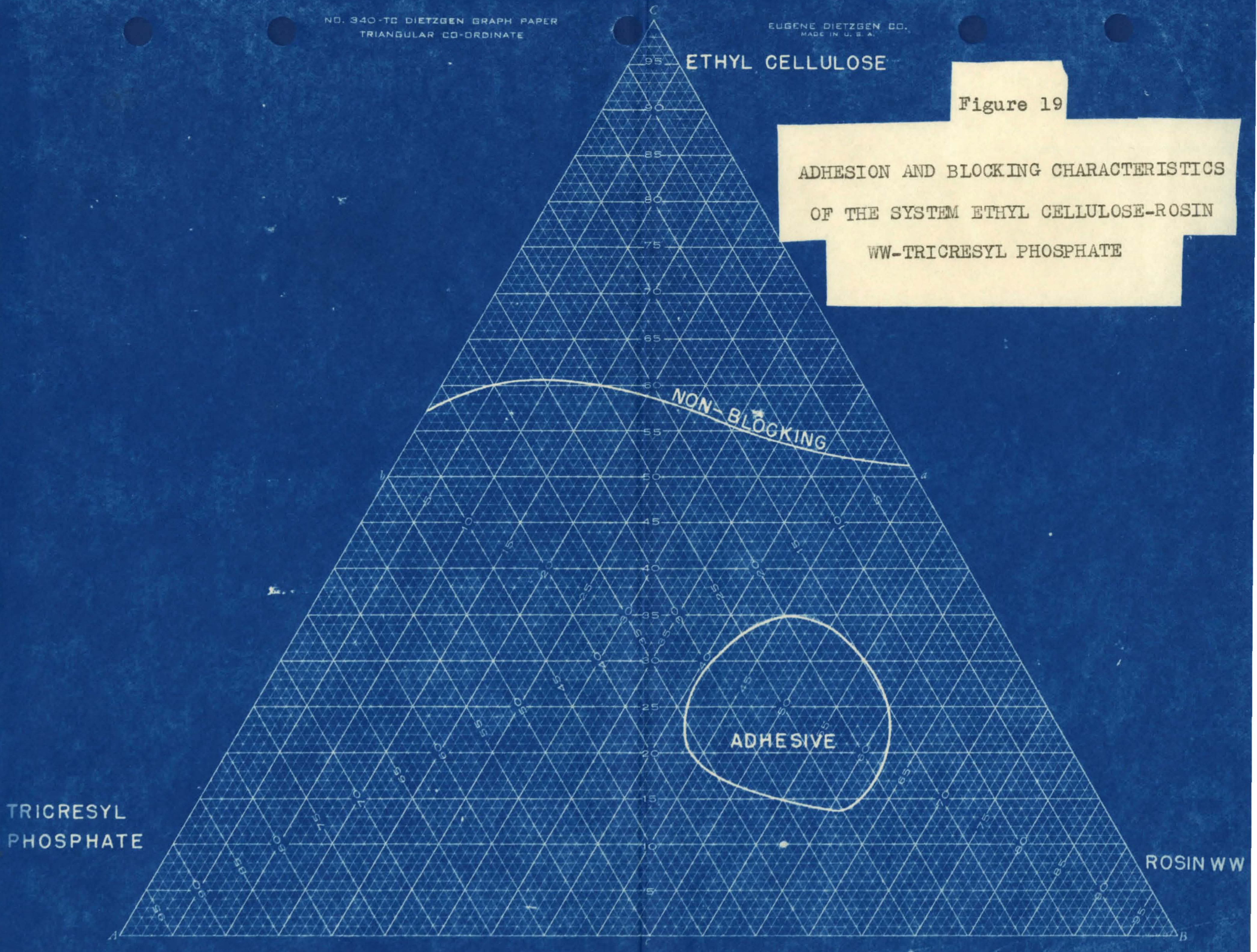


Figure 19

ADHESION AND BLOCKING CHARACTERISTICS OF THE SYSTEM ETHYL CELLULOSE-ROSIN WW-TRICRESYL PHOSPHATE

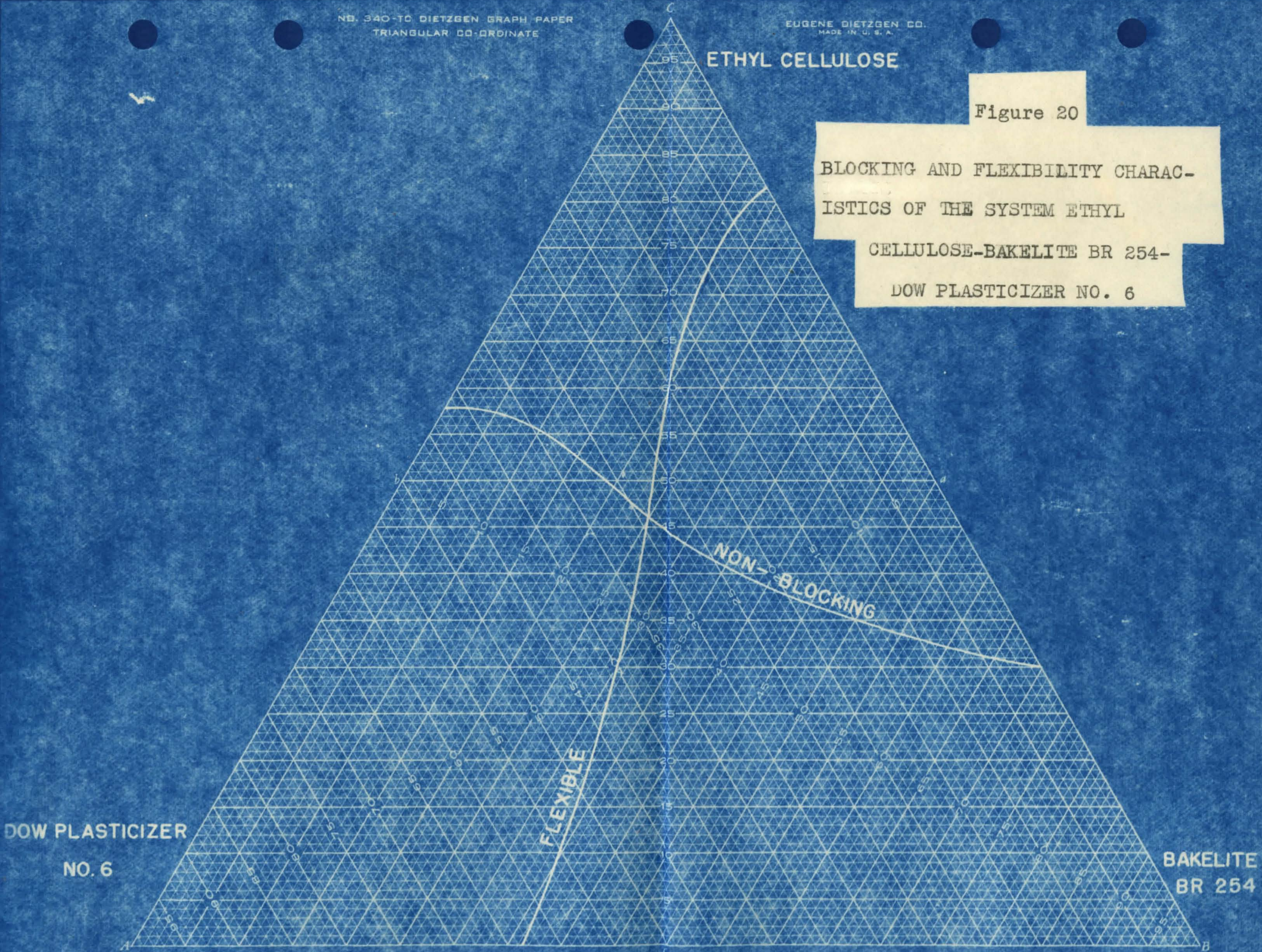


Figure 20

BLOCKING AND FLEXIBILITY CHARACISTICS OF THE SYSTEM ETHYL CELLULOSE-BAKELITE BR 254-DOW PLASTICIZER NO. 6

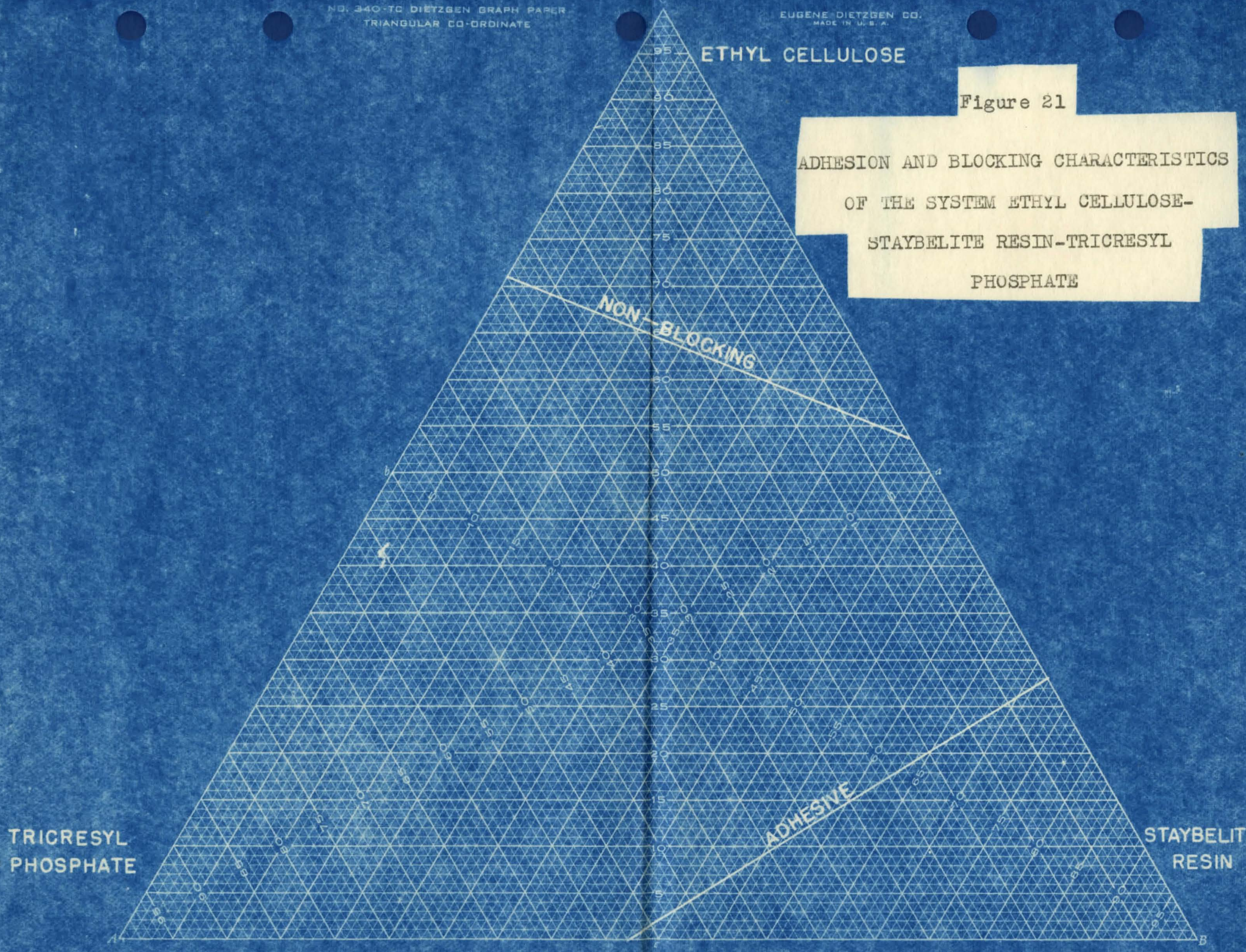


Figure 21

ADHESION AND BLOCKING CHARACTERISTICS OF THE SYSTEM ETHYL CELLULOSE-STAYBELITE RESIN-TRICRESYL PHOSPHATE characteristics.

The following is a description of the properties of these three systems:

(1) The ethyl cellulose-Arochlor 1262 system produced strong seals. Tearing bonds were made with aluminum foil, glassine paper, cellophane, and other packaging papers. Bonding lacquers of this system is easily accomplished at 150°C.

To produce tearing bonds these lacquers must contain more than 20% Arochlor 1262. Lacquers containing less than 20% of the Arochlor resin are non-blocking under the specified test conditions. All formulations of the system passed the flexibility requirements. The best combination of adhesion and blocking characteristics in the system is found in the lacquer containing

ethyl cellulose ----- 75.0%
Arochlor 1262 ------- 25.0%

The necessary solvent ratio was 5 cc of the 70-30% toluene-ethanol mixture per gm. of solids. This lacquer will pass the block test only if the temperature requirement is lowered to 40°C.

Carnauba wax was added to make the lacquer non-blocking at the specified 50°C. The formulation then becomes

ethyl cellulose ----- 74.6%

Arochlor 1262 ------- 25.0%

Carnauba wax -------- 0.4%

In order to dissolve the wax, it is necessary to heat the lacquer to the boiling point of the toluene-ethanol solvent mixture.

The final ethyl cellulose-Arochlor-wax combination seals with tearing bonds, is non-blocking, transparent, and flexible. Table II lists the formulations of the systems that were tested and rates the adhesion, blocking, and flexibility properties of each.

(2) The system ethyl cellulose-Dow resin 276-V2-tricresyl phosphate also gave good results. Seals of tearing bond were made from lacquers of this system to all the materials listed in Table V. The blocking resistance developed in this system is greater than that of the Arochlor formulation. Since the Dow resin is itself a liquid, all formulations of the system are flexible. Figure 14 shows the adhesion, blocking, and compatibility characteristics of this system.

A formulation of

ethyl cellulose ----- 55.0%

Dow resin 276-V2 ---- 30.0%

tricresyl phosphate - 15.0%

best combined the properties of adhesion and non-block. A solvent ratio of 4 cc of solvent per gm. solids is sufficient to bring this lacquer to the proper viscosity.

Carnauba wax was added to this system to raise its blocking temperature. With the wax addition the formulation becomes

ethyl cellulose ------ 55.0%
Dow resin 276-V2 ----- 30.0%
tricresyl phosphate -- 14.7%
carnauba wax --------- 0.3%

This lacquer will be referred to as HS-148.

Samples of HS-148 were subjected to the cold storage, aging, and machine tests described earlier. No loss of properties was noted in the films after 24 hours contact with dry ice and 30 days in the freezing compartment of an electric refrigerator. The aging test was run on this formulation for 5 months. No loss in adhesion, non-block, or flexibility was noted.

The cork tipping and package seals made with HS-148 in the Brown and Williamson plant were compared to the same seals made with regular industrial adhesives. In the case of cork tipping 300 seals were tested. Table VI lists the result of this testing. 88% of these seams were tighter and more durable than the regular seal, 7% were not as good as the regular seal, but no difference could be detected in the remaining 5%. The foil-to-foil seams made on the all-metal package were rated in comparison with packages made with the regular adhesive. Little or no difference could be detected between the seals of HS-148 and those of the regular lacquer.

An attempt to substitute Dow Plasticizer No. 5 for tricresyl phosphate resulted in the following formulation which will be referred to as HS-196:

ethyl cellulose -------- 45.0%
Dow resin 276-V2 ------- 40.0%
Dow plasticizer No. 5 -- 14.7%
Carnauba Wax ----------- 0.3%

Toluene was found to be the best solvent for this material. Films of HS-196 adhere with tearing bonds to the materials listed in Table V. They are flexible and transparent. The carnauba wax addition makes it possible for HS-196 films to pass the blocking test. Under extreme cold, lacquers of this formulation became brittle but did not lose adhesion. An aging test of two months showed no change in the properties in films of HS-196.

Figure 15 shows the adhesion, blocking, and compatibility characteristics of this system.

## TABLE I

Adhesion, Blocking, and Flexibility Characteristics of the Formulation of Each System Best Combining These Properties.

| System | Adhesion | Blocking | Flexibility |
|---|---|---|---|
| Ethyl cellulose-Dow Plasticizer No. 6 | good | poor | good |
| Ethyl Cellulose-Arochlor 1262 | good | good | good |
| Ethyl Cellulose-Bakelite XR 14987 | poor | poor | good |
| Ethyl Cellulose-Nevillac S-Arochlor 1262 | fair | fair | good |
| Ethyl Cellulose-Bakelite 254-Dow Plasticizer No. 6 | poor | good | good |
| Ethyl Cellulose Super Beckacite 1001-Dow Plasticizer No. 6 | poor | good | good |
| Ethyl Cellulose-Tricresyl Phosphate-Rosin WW | fair | fair | fair |
| Ethyl Cellulose-Tricresyl Phosphate-Staybelite Resin | good | poor | good |
| Ethyl Cellulose-Poly Pale Resin-Bakelite XJ 15330 | poor | good | fair |
| Ethyl Cellulose-Dow Resin 276-V2-Tricresyl Phosphate | good | good | good |
| Ethyl Cellulose-Dow Resin 276-V2-Dow Plasticizer No. 6 | good | good | good |

## TABLE II

### Adhesion, Blocking, and Flexibility Characteristics of the System Ethyl Cellulose-Arochlor 1262

| Composition Wt. % | | Properties | | |
|---|---|---|---|---|
| Ethyl Cellulose | Arochlor 1262 | Adhesion | Blocking | Flexibility |
| 20 | 80 | poor | poor | good |
| 30 | 70 | poor | poor | good |
| 40 | 60 | poor | poor | good |
| 50 | 50 | fair | poor | good |
| 60 | 40 | fair | fair | good |
| 70 | 30 | good | good | good |
| 80 | 20 | fair | good | good |
| 90 | 10 | poor | good | good |

## TABLE III

### Adhesion, Blocking, and Flexibility Characteristics of the System Ethyl Cellulose-Dow Plasticizer No. 6

| Composition Wt. % | | Properties | | |
|---|---|---|---|---|
| Ethyl Cellulose | Dow Plast. No.6 | Adhesion | Blocking | Flexibility |
| 20 | 80 | poor | poor | good |
| 30 | 70 | poor | poor | good |
| 40 | 60 | fair | poor | good |
| 50 | 50 | good | fair | good |
| 60 | 40 | fair | fair | good |
| 70 | 30 | poor | good | good |
| 80 | 20 | poor | good | good |
| 90 | 10 | poor | good | good |

## TABLE IV

Adhesion, Blocking, and Flexibility Characteristics of the System Ethyl Cellulose-Bakelite XR 14987

| Composition Wt. % | | Properties | | |
|---|---|---|---|---|
| Ethyl Cellulose | XR 14987 | Adhesion | Blocking | Flexibility |
| 20 | 80 | poor | poor | good |
| 30 | 70 | poor | poor | good |
| 40 | 60 | poor | poor | good |
| 50 | 50 | poor | poor | good |
| 60 | 40 | poor | fair | good |
| 70 | 30 | poor | fair | good |
| 80 | 20 | poor | good | good |
| 90 | 10 | poor | good | good |

## TABLE V

Materials to Which Formulations HS-148 and HS-196 Were Sealed

| | | |
|---|---|---|
| Aluminum Foil | Glass | Cigarette Paper |
| Magnesium Sheeting | Celluloid | Steel and Iron Plate |
| Cellophane | Wood | Low Grade Papers |
| Bond Paper | Cork | Ethyl Cellulose Sheeting |
| Glassine Paper | Cardboard | Vinyl Sheeting |

## TABLE VI

### Comparison Between Cork Tipping Seams Made With HS-148 and Those Made With the Regular Industrial Adhesive

| Better than regular seam | Not as good as regular seam | No apparent difference | Total |
|---|---|---|---|
| 264 | 21 | 15 | 300 |

## DISCUSSION

Three lacquers have been formulated that fulfill the physical requirements for a heat sealing agent. No reference had been made, however, to toxicity. The problem requirements state that a film to be applied to the packaging of food and related products must be free from toxic effects.

The following is a discussion of the toxicity present in each of the three proposed lacquer formulations:

(1) The lacquer containing Arochlor 1262 has a marked toxic effect on everything with which it comes in contact. The toxic nature of this lacquer is entirely due to the Arochlor 1262. Arochlor 1262 has a strong corrosive effect on human tissue. Extended contact with the heavy liquid causes deep burns. Fumes of this resin are sharp and acrid. If drawn into the lungs they cause smarting and coughing.

Lacquers containing such toxic constituents can not be recommended for use in the packaging of foods. Its effect on human skin make even the manufacture of such lacquers quite dangerous.

(2) Lacquer HS-148 contains ethyl cellulose, Dow resin 276-V2, tricresyl phosphate, and carnauba wax. With the exception of tricresyl phosphate, none of these constituents possess detectable toxicity.

A letter to the Monsanto Chemical Company of St. Louis, Missouri, concerning the toxicity of tricresyl phosphate made by them brought the following reply from Dr. R. E. Kelly, Medical Director: "The tricresyl phosphate manufactured by us contains less than two per cent of the ortho isomer. The ortho isomer has been incited as the toxic element of tricresyl phosphate, but I do not believe it can be said that even a meta para mixture possesses no toxicity.

"The advisability of using tricresyl phosphate as a coating to be applied in the food packaging industry would depend on whether or not this material could be abstracted from the coating by the food. If such a situation could be present we would not advise its use as we think that even a low ortho isomer tricresyl phosphate possesses toxicity."

The information in Dr. Kelly's letter indicated that, although containing only 14.7% tricresyl phosphate, HS-148 possesses a potential toxicity. Since the lacquer itself is never applied in direct contact with food, it is quite doubtful that this toxic effect would be felt. The only guarantee of safety, however, would be the actual testing of this lacquer in contact with the food to be packaged.

(3) HS-196 contains ethyl cellulose, Dow resin 276-V2, and Dow plasticizer No. 5. All these materials are products of the Dow Chemical Company of Midland, Michigan. Mr.

K. D. Bacon of that company states that these three materials are entirely free from toxicity. From this information it can be stated that formulation HS-196 has no toxic effect and is, therefore, suited to application in the packaging of food and related products.

# CONCLUSIONS

Two lacquers have been formulated which meet the problem specifications. Both are clear, flexible films which form tearing bonds with aluminum foil, glassine paper, cellophane, and other packaging papers. Each is non-blocking at 50 degrees C. under 1 psi.

HS-148, composed of

ethyl cellulose ------ 55.0%
Dow resin 276-V2 ----- 30.0%
tricresyl phosphate -- 14.7%
carnauba wax --------- 0.3%

has better adhesion and blocking characteristics than has HS-196. For this reason HS-148 is recommended as the best formation for general heat sealing application.

HS-196, composed of

ethyl cellulose ------ 45.0%
Dow resin 276-V2 ----- 40.0%
Dow plasticizer No.5 - 14.7%
carnauba wax --------- 0.3%

is free of all toxicity. For this reason it is recommended for application where contact with food products is unavoidable.

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through a fellowship grant
by the Dow Chemical Company
to the
University of Louisville Department of Chemical Engineering

# APPENDIX

MATERIALS:

RESINS

| Name | Type | Manufacturer |
|---|---|---|
| Arochlor 1262 | Chlorinated Diphenyl | Monsanto Chem. Co. |
| Bakelite BR 254 | Phenolic | Bakelite Corp. |
| Bakelite XR 14987 | Phenolic | Bakelite Corp. |
| Bakelite XJ 15330 | Modified Phenolic | Bakelite Corp. |
| Nevillac S | Coumarone-Indene | Neville Co. |
| Poly Pale Resin | Hydrogenated Rosin Ester | Hercules Powder Co. |
| Resin 276 V2 | Styrene Derivative | Dow Chemical Co. |
| Rosin W W | Natural Rosin | Hercules Powder Co. |
| Staybelite Resin | Natural Rosin Ester | Hercules Powder Co. |
| Super Beckacite 1001 | Phenolic | Reichold Chemicals Inc. |

PLASTICIZERS

| Trade Name | Chemical Name | Manufacturer |
|---|---|---|
| Dow Plasticizer No. 5 | Diphenyl Monophosphate | Dow Chemical Co. |
| Dow Plasticizer No. 6 | Dimonophenyl Phosphate | Dow Chemical Co. |
| Flexol DPO | Polyethlene Glycol Di-2-Ethylhexoate | Carbide & Carbon Chemicals Corp. |
| Santicizer B16 | Butyl Phthalyl Butyl Glycollate | Monsanto Chemical Co. |
| Tricresyl Phosphate | Tricresyl Phosphate | Monsanto Chemical Co. |

# VITA

The author was born in Jackson, Mississippi, on September 18, 1924. His father, William Black Moore, and mother, Mai Isom Whitten Moore, were native to Mississippi. Both are of Scotch-Irish ancestry.

Until the age of three, the author lived in Jackson, Mississippi, moving in 1927 to Greenville, South Carolina. He, at four years, entered a private school, transferring to Haynes primary school two years later. In 1931 his family returned to Jackson, where he was then entered in Power School. From here he progressed to Bailey Junior High in 1937. After two years in junior high, the author began his high school training in Central High at Jackson.

The author attended Mississippi State College in Starksville, Mississippi, following his high school graduation in 1942. His training in Chemical Engineering at Mississippi State came to an end in 1943 when he was called into the Navy V-12 program at the University of Louisville. There he continued work toward fulfilling the requirements for the degree of Bachelor of Chemical Engineering. The degree was awarded in February, 1945.

On May 5, 1945, the author was commissioned Ensign, CEC, USNR, and was immediately sent to Manila, P. I., to join the Thirty-fifth Naval Construction Battalion. He was retired to inactive reserve status in July, 1946.

Mr. Moore was married to Miss Lillian Wells on September 14, 1946. Mrs. Moore, the daughter of Anne Ramsey Longino and John Thomas Wells, was born in Greenwood, Mississippi.

In order that he might work toward the degree of Master of Chemical Engineering the author re-entered the University of Louisville on October 1, 1946. At this time he received the Dow Fellowship. With the acceptance and subsequent publication of this thesis in September, 1947, he will receive the degree of Master of Chemical Engineering.