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DEVELOPMENT OF SILICONE RUBBERS FOR USE AT TEMPERATURES DOWN TO -100°F.

U.S. GOVERNMENT CONTRACT W-44-109-QM-2161

PROGRESS REPORT 1

CONNECTICUT HARD RUBBER COMPANY

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Connecticut Hard Rubber Co. New Haven, Conn.

(6) DEVELOPMENT OF SILICONE RUBBERS FOR USE AT TEMPERATURES DOWN TO -100°F. New
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SUMMARY

Silicone rubbers, which appear to be one of the most promising types of rubber for low-temperature use, have been available commercially for several years. The rubbers currently available do not have sufficient tensile strength, abrasion resistance, etc., to be considered as possible substitutes for hydrocarbon rubber in many applications. The immediate problem undertaken in the present work is essentially one of reinforcing this type of rubber with suitable pigments. The long-range problem is one of adapting reinforced silicone rubbers to service at low temperatures (down to about -100°F).

A survey of the possible methods of attack on this problem led to the conclusion that attention should be focused on the interface between the pigment and rubber. Although it is realized from studies on hydrocarbon rubbers that the conditions existing at this interface may be the most important factor determining the extent of reinforcement relatively little knowledge regarding this feature of rubber-pigment systems is available. It appears firmly established that the characteristics which predominate in determining the nature of the interface conditions are:

1. Particle size
2. Particle shape
3. Particle surface
   a. Extent
   b. Nature
4. Nature of the rubber-pigment bond.

Essentially two theories of rubber reinforcement have been proposed. In one case the pigment-rubber bond is considered to be a case of purely physical adsorption, involving either adsorption of a wetting agent by the pigment or direct adsorption of rubber on the pigment. In the other case it is considered that reinforcement involves chemical reaction at the rubber-pigment interface. The nature of such reaction is ill-defined but it has been considered by some workers to be a type of vulcanization with cross-linkages being formed on the pigment surface. A

survey of the literature on hydrocarbon rubber reinforcement reveals the experimental difficulties which arise in studying the nature of the interface. These difficulties are so great that despite a considerable volume of work there is as yet no single, unified theory of rubber reinforcement.

The experimental program must therefore be planned in such a way as to recognize that any of the prevailing theories may ultimately prove to be correct. For this reason the exploratory experimental program which is outlined has been planned to include the following:

1. Particle size and shape will be studied in the exploratory program by using at least five pigments of varying nature.
2. The nature of the pigment surface will be studied by using the pigments in three forms:
    a. As received
    b. Pretreated in air at 400°C.
    c. Pretreated in vacuum (10^{-4} mm.) at 1000°C.
3. Several special wetting agents will be used.
4. The vulcanization theory of reinforcement will be explored by depositing benzoyl peroxide (and perhaps other peroxides) on the pigments from solution.

The results of milling, curing and testing about 75 batches of silicone rubber are discussed briefly. These preliminary experiments served to familiarize the staff with the compounding of silicone rubbers. Consistency in results is now being obtained. The program outlined in the report is now underway and proceeding satisfactorily.

The equipment which will be used on this project, all of which has been assembled and is now being used, is described.

I. INTRODUCTION

A few years ago the General Electric Company and Dow-Corning Corporation announced almost simultaneously the commercial production of a new type of polymeric material called silicones. The products which have appeared on the market so far have been polymers containing the basic unit:

$$\begin{array}{c} CH_3 \\ -Si-O- \\ CH_3 \end{array}$$

The polymers are available in the form of oils, greases and rubbers.

The numerous interesting applications of these polymers need not be outlined here. The particular property of interest in the current work is the resistance to heat and cold. These materials are useful at temperatures well above the maximum temperatures at which hydrocarbon compounds are stable for long service periods. This property is perhaps the most important one from the point of view of developments to date. An equally interesting property, however, is the resistance of these materials to low temperature. It is believed that the basic polymer would be useful in rubber compounding, specifically, at temperatures as low as -100°F., well below the minimum temperature at which hydrocarbon rubbers function satisfactorily. The primary difficulty hindering development in this direction is a lack of knowledge regarding the reinforcement of silicone rubbers to provide reasonable tensile strength, elasticity, hardness and abrasion resistance.

Since a rubber which would function satisfactorily at temperatures as low as -100°F would be of great utility, this project was undertaken for the specific purpose of adapting silicone rubbers to such service. At the beginning of the work, however, the general problem of reinforcing silicone rubber will receive primary attention since there would seem to be no necessity for cold testing until more satisfactory results are obtained at ordinary temperatures. The compounded rubbers which are available commercially at the present time are a great improvement over those available only three years ago but they are still far below hydrocarbon rubbers in tensile strength, abrasion resistance, etc.

A decision as to the first method of attack to be followed in this work has

been reached as a result of several conferences between members of the technical staff of Connecticut Hard Rubber Company and three members of the teaching staff of Yale University who are devoting some time to the work. The former group, with a considerable amount of experience in the compounding of both hydrocarbon and silicone type rubbers, felt that the most important feature of silicone rubber-pigment systems which needed investigation and which offered most promise was the nature of the rubber-pigment interface. The latter group surveyed the literature on rubber reinforcement and reached the same conclusion. It was therefore decided that the first method of attack on the problem at hand would be an investigation of the nature of the rubber-pigment interface. The attack will be a direct one; i.e. the pigment surface will be treated by various means and then the pigment will be compounded with a silicone gum and tested.

The exploratory experimental program outlined in this report will be sufficient to indicate whether the first method of attack is a logical one. Any promising results obtained will be followed by more intensive investigation. Should the results indicate no marked success other methods of attack will be followed.

II. LITERATURE SURVEY

It may be supposed that the general methods of attacking the problem of reinforcing silicone rubber could be outlined with some degree of confidence if there were available a general theory for the reinforcement of hydrocarbon rubbers. Despite the development of numerous experimental techniques and the accumulation of a considerable body of experimental data, however, there has not as yet been developed a single, unified theory of reinforcement. On the contrary, each of the several theories finds some support in experimental evidence. The development of a general theory requires either the correlation of apparently conflicting data or a critical evaluation of the experimental techniques.

This situation demands that a program for development of a reinforced silicone rubber be formulated in such a way as to recognize the possibility that any one of the theories of reinforcement may be correct or that a general theory might be developed which would include some features of several of the current theories. For this reason there has been prepared a brief survey of the literature or rubber reinforcement. This review is critical rather than comprehensive and includes only a few articles selected because they seemed to represent the current views on the subject of reinforcement and to represent the current experimental techniques used in this field.

Characteristics of Reinforcing Pigments.

There has been a great deal of work done on the problem of determining the characteristics of reinforcing pigments which are responsible for or which contribute to the reinforcing action of the pigment. Shepard, Street and Park (1) have ably reviewed the literature on this subject through 1936. Beyond that date, numerous articles concerned with the characteristics of reinforcing pigments have appeared and a few of these are included in the discussion which follows .

There seems to be general agreement that particle size is one of the most important pigment characteristics related to reinforcing properties but that it is not the unique factor responsible for reinforcement. In general, it appears that reinforcement of hydrocarbon rubbers is successfully accomplished by pigments having

a particle diameter considerably less than 1 micron, although fine subdivision is not in itself a guarantee of reinforcing power. Some finely-divided pigments, such as lithopone, show practically no reinforcing power. This lack of reinforcing power might be due to the nature of the pigment surface or to poor distribution in the rubber.

Particle shape appears also to have a bearing on reinforcing properties of pigments but its effect is again not well defined. Most of the reinforcing pigments used in compounding hydrocarbon rubbers are isotropic (three main axes of approximately equal length). Anisotropic substances (such as plates or rods) do not in general exhibit reinforcing power. Aside from these conclusions little knowledge is available regarding the effect of particle shape on reinforcing power. It is to be hoped that use of the electron microscope will provide further information on this point.

That particle surface also has a definite effect on reinforcing power is also well established. The extent of the particle surface is known to be of importance although it may be pointed out that it is the extent of the particle surface which is in contact with rubber that is of primary importance. Referring again to lithopone, it has been thought that the failure of this material to reinforce rubber (despite the fact that the particle size is small, the particle shape isotropic and the particle surface comparable in magnitude to that of carbon black) may be due to the difficulty of dispersing this material in rubber. Special milling techniques which accomplish better dispersion do, in fact, improve the performance of this pigment.

The nature of the particle surface may also have a direct bearing on reinforcing power. Attempts have been made to indicate variations in the nature of the particle surface by pH measurements (2) This provides little information on the true nature of the surface but is a convenient method of indicating variations. Heats of adsorption have also been used as a measure of the activity of the particle surface but the data are too limited to permit reaching definite conclusions as to the reliability of this method. The third method of evaluating the effect of the

nature of the surface on reinforcement involves subjecting the pigment to various pre-treatments intended to alter the nature of the surface and then testing the pigment in an actual rubber formulation. Barnett and Jones (3) have published a study concerned with this factor. Basic zinc carbonate, for example, is definitely improved in reinforcing characteristics by calcination at temperatures below 350°C. Heating to temperatures above this value, however, resulted in a decrease in reinforcing power. Unfortunately, it cannot be determined how much of the change in reinforcing power is due to a change in the nature of the surface. In the first place, some decomposition of the basic zinc carbonate occurs on heating. Secondly, electron micrographs show a definite decrease in particle size resulting from heating to 350°C. and a definite agglomeration occurring after heating to higher temperatures. Thus the results can be interpreted in terms of particle size alone. It would be highly desirable to extend this study to other pigments.

To summarize, the reinforcing power of pigments in hydrocarbon rubbers is influenced to some extent by particle size, particle shape and extent of the particle surface. The nature of the particle surface is also a factor. Quantitative conclusions regarding the effects cannot be drawn from present data.

Characteristics of Rubber - Pigment Systems.

It has been supposed in the past that an ideal system for reinforcement of rubber would be one in which the individual pigment particles are separated from all other pigment particles by a thin film of rubber. That this condition is not satisfied in any commercially feasible process nor in any known laboratory technique seems to have been established beyond doubt, this being the one point on which all experimental techniques are agreed. Recently there has been expressed some opinion that such a system, even if it could be realized, might not be the ultimate in rubber reinforcement (4). The other extreme picture of a rubber-pigment system would be one in which the pigment particles are in contact to form a three-dimensional grouping, actual contact between rubber and pigment being limited to a relatively small part of the pigment surface. Actual rubber-pigment systems apparently contain both individual pigment particles and clusters of pig-

ment particles. The relative value of these two types of pigment dispersion (individual particles vs. clusters) has not been established.

Granting, then, that a rubber may be successfully reinforced by a pigment existing both as individual particles and as clusters it is next necessary to inquire into the nature of the bond between pigment and rubber. Most invest -igators have viewed this bond as a case of physical adsorption while others believe that true chemical bonds are involved. The answer to the question of which type of bond is actually involved has not been obtained. It appears likely that an answer to this problem would provide a starting point for a general theory of rubber reinforcement. Unfortunately, no experimental technique that has been used so far has provided this answer.

Experimental Techniques for Studying Rubber-Pigment Systems.

A truly satisfactory experimental technique for studying rubber-pigment systems would provide information on the degree of dispersion of the pigment and on the nature of the bond between pigment and rubber. Satisfactory techniques for determining the degree of dispersion are available but the nature of the pigment-rubber bond remains to be determined. A brief review of some of the techniques is given below and some of the conclusions reached are also listed. The review is by no means complete. In each case, only one or two references are listed. A complete review would involve many more references.

1. Optical Microscope.

The optical microscope was one of the earliest tools applied to the study of rubber-pigment systems. This technique supplied a fairly good estimate of the size of the pigment particles but very little information about particle shape. Applied to pigment-rubber systems, it was moderately successful in determining the degree of pigment dispersion. Gronquist (5), for example, determined that during curing there occurs a flocculation of previously dispersed particles.

2. X-Ray Diffraction Patterns.

Gehman (6) has published a comprehensive review of general x-ray

diffraction phenomena for rubber. This technique essentially makes possible studies which cannot be undertaken with the optical microscope but its usefulness is somewhat limited by the fact that a crystal structure is required. This condition may be satisfied in studies of rubber by stretching of the rubber. Thus, Gehman and Field (7) report a study of pigment-rubber systems at 400% elongation. They conclude that their results bear out the theory that reinforcement is a type of vulcanization insofar as carbon black is found to assist crystallization of the rubber on stretching just as vulcanization assists the crystallization on stretching of milled rubber by the reduction in plasticity. Aside from this one indication, their results can not be said to offer support for the vulcanization theory.

3. Electron Microscope

This powerful tool for study of rubber-pigment systems has not yet been utilized to any great extent in such studies. Properly applied, it supplies a great deal of information on the particle size and shape (8) and on the degree of dispersion. For example, it has been used to show that chain structure is characteristic of most forms of reinforcing black and that this structure persists after milling. Chain structures in vulcanized rubber are indicated to be segments of chains originally of greater length.

4. Electrical Resistance Studies.

The electrical resistance of rubber compounds containing black as the reinforcing pigment provides some information on the nature of the dispersion. Thus a system in which complete dispersion existed would be expected to have a higher resistance than a system in which carbon chains predominated. Parkinson and Blanchard (4) have applied this technique to show that resistivity changes occurring in unvulcanized rubber on heating and cooling are completely reversible, suggesting that heat does not promote a permanent change in the arrangement of the carbon particles.

Milling increases the resistance irreversibly, presumably as a result of breaking the carbon black chains.

5. Solubility Studies.

It has been noted that the limited portion of highly loaded channel black-rubber stocks which will dissolve in such solvents as benzene does not in general carry with it any black from the stock. This suggests that reinforcement may involve (1) strong physical adsorption, (2) a selective adsorption of the higher-molecular-weight fractions of the rubber, these being in general the least soluble portions of the rubber, or (3) a sort of vulcanization occurring at the pigment-rubber interface. Solubility studies alone do not distinguish between these possibilities.

Another technique for using solubility studies involves dissolving rubber in a solvent such as toluene and then adding the pigment to the solution. After equilibrium has been established the unadsorbed fraction may be recovered by centrifuging. The adsorbed fraction may be recovered in part by allowing the pigments to stand for several days in a large volume of toluene and then centrifuging again. Recovery of final traces of organic material from the pigment is not always possible. In the case of an acid-soluble pigment such as magnesia, however, dilute hydrochloric acid may be used to dissolve the pigment and organic matter can be extracted with ether. Barnett and Jones (3) applied this technique to systems involving GR-S and various pigments (magnesia, calcium silicate, channel black) and concluded that adsorption of GR-S by these pigments is not selective. Goldfinger (9) finds, however, that carbon black does selectively adsorb certain fractions of GR-S.

6. Swelling Properties.

Dannenberg (10) has noted that equilibrium-swelling measurements of high-polymer compositions are sensitive to the presence of primary-valence bonds which can function as chemical cross-linkages but are not affected by the weaker forces of physical adsorption. His results indicate that

the bond between GR-S and black is not of a chemical nature but is rather an adsorptive force of the van der Waals type.

Theories of Reinforcement.

The interaction which occurs between rubber and pigment in reinforcement has been the subject of numerous studies since it has long been realized that establishing the nature of this interaction might provide the basis for a general theory of reinforcement. This is one of the most interesting problems of rubber chemistry and at the same time one of the most difficult. The current theories are reviewed briefly below and some of the experimental indications are outlined.

One picture of the interaction between rubber and pigment involves purely physical adsorption, depending on van der Waals type adsorptive forces. Experimental proof of this theory is difficult to establish although there are a few results which support it. Thus it has been contended that wetting agents such as stearic acid are necessary for successful milling of hydrocarbon rubbers and pigments. If such wetting agents do serve a useful function in milling it would appear that the case of physical adsorption involved might be one in which the stearic acid is adsorbed on the pigment by the polar carboxyl group and the hydrocarbon portion of the stearic acid is dissolved in the rubber matrix. An attempt has been made to establish this by calculating the amount of stearic acid which would be required to cover the carbon black with a monomolecular layer. The actual quantity of stearic acid required for incorporation of pigment in the rubber is only about one-fourth of this calculated quantity. This result seems to be reasonable in view of the fact that it has been clearly indicated that the contact between rubber and black does not involve the entire surface of the black because the pigment exists to some extent in clusters. This selective adsorption of the wetting agent is supported to some extent by the data of Barnett and Jones (3) on the composition of material adsorbed on magnesia, calcium silicate and carbon black when these pigments are contacted with a rubber cement. Adsorption on magnesia and calcium silicate particularly shows a selective adsorption of fatty acids. With carbon black the distribution of fatty acid was found to be non-selective. Morris and Hollister (11) have objected to the

theory of wetting agents as outlined above. These workers state that the solubility of fatty acids in rubber is of the order of magnitude of the concentration found necessary for milling and that these acids can not therefore be adsorbed appreciably. This argument seems to be without basis since the equilibrium concentration of fatty acid in rubber in the presence of a strong adsorbing agent would be well below the solubility. The experimental results of these workers do indicate quite clearly, however, that paraffin wax may be substituted for stearic acid in compounding butyl rubber. They conclude that the effect of stearic acid (or paraffin wax) is merely one of softening the rubber, making milling easier. A similar study with other types of rubber should be made. Another argument for the wetting agent theory lies in the fact that there appears to be a rough correlation between heat of wetting of a pigment by stearic acid and reinforcing properties. Other indications of a simple physical picture of reinforcement are obtained by studies outlined below concerned primarily with chemisorption.

Other workers have contended that primary valence bonds are involved in the rubber-pigment bonds. Reinforcement may be considered as a type of vulcanization in this case, the primary valence bonds of cross-linkage being formed at the pigment-rubber interface. Several experimental indications that this may be the case are available. Thus it has been found that if a hydro carbon rubber be compounded with an acid-soluble pigment, leaching of the pigment will leave a rubber which has undergone a distinct increase in viscosity and a decrease in solubility as compared with the original stock. Maunton and Waring (12) assumed that the change might be due to an oxidation vulcanization and reasoned that carbon black treated with chlorine should show an improvement over ordinary carbon black because of the chemical reactivity of chlorine. This was found to be the case. Park (13) has obtained experimental results which agree with this theory and is inclined to the belief that adsorbed oxygen may be the vulcanizing agent. Gehman and Field (7) report x-ray diffraction data which support the idea of reinforcement as a type of vulcanization in that black assists crystallization of rubber on stretching just as vulcanization assists the crystallization on stretching of milled rubber by the

reduction in plasticity. Dannenberg (10) attempted to apply equilibrium-swelling measurements of rubber compositions to this problem, noting that such measurements are sensitive to the presence of primary-valence bonds. The results do not indicate the presence of such bonds but Dannenberg points out that the sensitivity of the method may not be great enough.

1. Shepard, Street and Park, Fillers and Reinforcing Agents, (Chapter XI of Davis and Blake's Chemistry and Technology of Rubber, Reinhold Publishing Corporation, New York, 1937)

2. Braendle, Steffen and Sheppard, India Rubber World, 119, 57, 62, 74, (October, 1948)

3. Barnett and Jones, Ind. Eng. Chem., 41, 1518 (1949).

4. Parkinson and Blanchard, Trans. Inst. Rubber Ind., 23, 259 (1948).

5. Grenquist, Ind. Eng. Chem., 20, 1073 (1928); 21, 665 (1929).

6. Gehman, Chem. Rev., 26, 203 (1939).

7. Gehman and Field, Ind. Eng. Chem., 32, 1400 (1940).

8. Columbian Carbon Co. Research Laboratories, Rubber Chem. and Tech., 14, 52 (1941)

9. Goldfinger, Rubber Chem. and Tech., 18, 286 (1945).

10. Dannenberg, Ind. Eng. Chem., 40, 2199 (1948)

11. Morris and Hollister, Ind. Eng. Chem., 40, 2325 (1948)

12. Naunton and Waring, Trans. Inst. Rubber Ind., 14, 340 (1939).

13. Park, Ind. Eng. Chem., 31, 1402 (1934)

III. EXPLORATORY EXPERIMENTAL PROGRAM

The general problem of reinforcing silicone rubber is considered in this work to be one of modifying by various means the nature of the pigment-rubber interface. For the present no attempt will be made to alter the nature of the gum. The nature of the pigment surface and the development of wetting agents are to receive primary attention.

For the purposes of a preliminary survey it is intended that the work follow the outline which is attached. This outline may be modified as the results become available, particularly if an interesting lead develops. Hence the program should be considered a tentative one, to be modified as dictated by experience.

It will be necessary in the preliminary survey to restrict the number of pigments studied. Other pigments will be included in later work after some of the suggestions have been explored. The pigments studied in the first part of this work will be:

1. A reinforcing black
2. Titanium dioxide (anatase), particle size less than 1 micron
3. Silica, Innis-Speiden 1240
4. Diatomaceous earth, Celite 505
5. Linde Silica

The reinforcing black is included because of the superior performance of this pigment in hydrocarbon rubbers. Blacks are not used at the present time in silicone rubber compounding because they destroy the effect of benzoyl peroxide. Hence this pigment can be used only if this effect can be eliminated. Some of the surface treatments proposed might accomplish this. Titanium dioxide is included because it has been successfully used in silicone rubber compounding. However, the particle size chosen for this work is well below that of titanias which have been used so far. The Innis-Speiden silica is chosen because of its successful use in silicone rubber compounding. Unfortunately, no information is available on the nature, chemical or physical, of this silica. Hence two other silicas are included. The Celite 505 is a silica product of well-defined physical properties

but of relatively large particle size. Linde silica has a much smaller particle size, being comparable to reinforcing blacks in this respect.

Among the pigments which are to be studied in later portions of this work are anatase titanias of varying particle size. The National Lead Co. (Titanium Division Research Laboratory) has supplied this material in particle sizes of 0.06-0.3 micron, 0.01-0.12 micron, 0.01-0.06 micron. It is intended to extend the range of particle sizes.

Since the whole attack on this problem is to be at first concerned with the nature of the pigment-rubber interface, it is considered that the nature of the surface of the pigment must be studied thoroughly. Each pigment will be tested in three forms. Obviously, the first form in which each pigment is used should be as received, this form serving primarily as a control. Next the pigments will be cleaned by subjecting them to a temperature of about 1000°C and a pressure of about 10^{-4} mm. hg. These extreme conditions should indicate with fair accuracy whether any gain in processing ease or in product properties may be expected as a result of activating the pigment surface. Should such a gain be noted it is suggested that activation of the pigment surface by heating to a lower temperature, 400°C, in air for one hour be tried. It is likely that in some cases this treatment will yield a pigment surface as active as that obtained by the more severe conditions. In all cases, the activation at 400°C will be used only if the first study indicates a real advantage due to the cleaning at 1000°C and 10^{-4} mm. Hg.

At the end of each section of the following outline a tabulation of experiments to be performed is included. The letters included in this tabulation serve merely to label the particular portion of the work.

A. WETTING AGENTS

On the basis of a study of the compounding of hydrocarbon rubbers it has been suggested that a logical attack on the silicone rubber reinforcement problem would be one concerned with the nature of the wetting agent. In the case of the hydrocarbon rubbers a satisfactory and relatively cheap wetting agent is available in

stearic acid. Apparently stearic acid is of no value in the case of silicone rubbers. If we accept the usual picture of the method by which stearic acid functions in processing hydrocarbon rubbers (strong adsorption of the carboxyl group on the pigment surface and solution of the hydrocarbon chain in the rubber matrix) then it may be supposed that the failure of stearic acid to function similarly in silicone rubber systems is due to one of the following:

a. The adsorption is not strong enough because of:

1. the nature of the polar group, or

2. the nature of the pigment surface

b. The hydrocarbon chain is not soluble in the silicone rubber.

It is proposed to test each of the indicated possibilities to some extent.

The nature of the polar group will be modified by using first an alkyl sulfonic acid instead of a fatty acid. It is proposed also to synthesize and test at least one silicone sulfonic acid with a structure of the type:

$$(CH_3)_3\,Si\text{-}O\left(\begin{array}{c}CH_3\\ |\\ Si\text{-}O\\ |\\ CH_3\end{array}\right)_x\begin{array}{l}CH_3\\ |\\ Si\text{-}C_6H_4SO_3H\\ |\\ CH_3\end{array}$$

The nature of the pigment surface is to be studied as noted previously (page 1).

Modifying the nature of the chain to which the polar group is attached will receive considerable attention. It is planned first to try some fatty acids of shorter chain length than stearic. This suggestion arises from the observation that silicone rubber is somewhat soluble in low molecular weight hydrocarbon such as gasoline but relatively insoluble in the higher molecular weight hydrocarbons found in such materials as lubricating oils. It is planned also to synthesize and test some carboxylic acids with silicone chains, such as:

$$(CH_3)_3\,Si\text{-}O\left(\begin{array}{c}CH_3\\ |\\ Si\text{-}O\\ |\\ CH_3\end{array}\right)_x\begin{array}{l}CH_3\\ |\\ Si\text{-}CH_2COOH\\ |\\ CH_3\end{array}$$

For each wetting agent tested, the following experiments will be necessary:

Pretreatment	Black	TiO_2	Silica 1240	Celite 505	Linde Silica
As received	WA-A-B	WA-A-T	WA-A-1240	WA-A-505	WA-A-L
1000°C, 10^{-4} mm	WA-1000-B	WA-1000-T	WA-1000-1240	WA-1000-505	WA-1000-L
400°C	WA-400-B	WA-400-T	WA-400-1240	WA-400-505	WA-400-L

The staff will synthesize the wetting agents which are not available. It is intended first to synthesize a silicone carboxylic acid by photochemical chlorination of a low-molecular-weight silicone oil, conversion to a Grignard type of compound and treatment with CO_2. The silicone sulfonic acid may be prepared by sulfonation of a silicone oil containing one phenyl group per molecule

B. BENZOYL PEROXIDE ON PIGMENTS

It has been suggested that a better bond between a pigment and silicone rubber might be obtained if the benzoyl peroxide which is necessary in processing were adsorbed on the pigment surface before milling and curing. Thus the benzoyl peroxide would perform its function (presumably to increase the silicone chain size) during milling and curing at the pigment-rubber interface. It has been hypothesized that a similar effect is necessary in the processing of hydrocarbon rubbers and that the agent responsible is adsorbed oxygen.

A survey of the available data on benzoyl peroxide indicates that it is most stable in aromatic solvents. A 0.2M solution in benzene at 30°C, for example, is about 10% decomposed in 300 hours. It might be possible to adsorb benzoyl peroxide on the pigment from benzene solutions but no data on benzoyl peroxide adsorption have been found. As a first approach to the problem, the pigment to be tested will be placed in a 0.2M solution of benzoyl peroxide in benzene. After one hour standing, some of the benzene solution will be decanted and analyzed to determine whether appreciable adsorption has occurred. If not, it will be necessary to remove the benzene by boiling, either at atmospheric pressure or at reduced pressure.

Pretreatment	Black	TiO_2	Silica 1240	Celite 505	Linde Silica
As received	BP-A-B	BP-A-T	BP-A-1240	BP-A-505	BP-A-L
1000°C, 10^{-4}mm.	BP-1000-B	BP-1000-T	BP-1000-1240	BP-1000-505	BP-1000-L
400°C	BP-400-B	BP-400-T	BP-400-1240	BP-400-505	BP-400-L

C. SILICONE FILMS ON PIGMENTS

It appears reasonable to expect that a silicone would be a logical bonding agent between a pigment and a silicone rubber, particularly in view of the fact that the silicone would be expected to be readily miscible with the gum. The nature of any bond which might exist between pigment and silicone is difficult to define. It does not appear reasonable to expect that this bond would be chemical in nature nor does it appear likely that there would be a strong adsorption of the silicone on the pigment. It becomes necessary to turn to the experience with silicone coating of ceramic forms in an effort to decide on a logical method of attaching the silicone film to the pigment. Two basic techniques are available, either of which is said to give a firmly-adhering silicone film.

Use of Silicone Oils

Silicone oils have been used to deposit a waterproof film on ceramics. A recommended procedure is:

a. Pretreatment of the solid (400°C, 1 hr.)

b. Cooling to 80 - 200°C

c. Immersion in a solution of a silicone oil in an aromatic solvent for a few seconds.

d. Draining

e. Baking at 160°C ± 5° for 2-4 hours.

For each silicone oil investigated the experiments are as follows:

Pretreatment	Black	TiO_2	Silica 1240	Celite 505	Linde Silica
400°C	SO-400-B	SO-400-T	SO-400-1240	SO-400-505	SO-400-L
1000°C, 10^{-4}mm	SO-1000-B	SO-1000-T	SO-1000-1240	SO-1000-505	SO-1000-L

Use of Volatile Silicone Compounds

The application of a silicone film may also be accomplished by pre-condition-

ing the material to be coated by exposing it to air at about 70°F with a relative humidity of 50-90%. The relative humidity is not a critical factor except that it must be below 100% to insure that no droplets of water are present on the surface. After the solid has reached equilibrium with the air it is exposed to the vapor of dimethyl silicon dichloride to form a film by hydrolysis on the surface.

It is proposed to use essentially this technique in the present work. When the pigment is pretreated by heating to 400°C in air, preconditioning of the sample will be carried out in a desiccator containing a salt solution of such concentration as to give a relative humidity in the proper range. The preconditioned material will then be transferred to a second desiccator, this one being provided with a stopcock. The vapor of dimethyl silicon dichloride will be passed into the desiccator through this cock.

When the pigment is treated by heating to 1000°C at 10^{-4}mm. it is intended to pre-condition the pigment by connecting the tube in which the pigment has been treated to a small glass flask containing a salt solution. This will be done without breaking the vacuum. After several hours of pre-conditioning the stopcock connecting to the water reservoir will be closed, and a second stopcock connecting to a tube of dimethyl silicon dichloride will be opened. During preconditioning the pressure in the system will be the vapor pressure of the salt solution. During treatment the pressure in the system will be the vapor pressure of dimethyl silicon dichloride.

Pretreatment	Black	TiO_2	Silica 1240	Celite 505	Linde Silica
400°C	S-400-B	S-400-T	S-400-1240	S-400-505	S-400-L
1000°C, 10^{-4}mm	S-1000-B	S-1000-T	S-1000-1240	S-1000-505	S-1000-L

It is suggested that it might be profitable to repeat these experiments using a mixture of dimethyl silicon dichloride (20 parts) and trimethyl silicon chloride (1 part) to deposit the film. This will effectively limit the chain length of the material constituting the silicon film.

IV. PRELIMINARY MILLING AND CURING OPERATIONS

General Program.

In the milling and curing operations carried out so far about 75 batches of silicone rubber have been processed. They have served the primary purpose of providing experience in silicone rubber compounding for the operators and have given the staff a first hand acquaintance with the behaviour of the gum and the pigments in the compounding process. In general, the early runs gave inconsistent results and the rubber was of poorer quality than expected from the results of other laboratories. With experience the consistency and quality have improved to a point where tensile strength, elongation and hardness values on several samples, compounded and cured in the same way, agree within 15% or less.

Ingredients.

The compounds have been based on 100 parts by weight of G.E. silicone gum 9979-G or G.E. silicone gum 81125 and 2 parts Laperco AS (95% benzoyl peroxide coated with stearic acid). Various fractions of filler have been added; however, we have now standardized tentatively on 25 parts of filler by volume per 100 parts of gum. The pigment loading has been standardized on a constant volume rather than constant weight basis in accordance with the general practice in hydrocarbon rubber compounding.

In some of the earliest work 1 part of lead oxide was added. This was discontinued on the advice of General Electric that it served no useful purpose.

A wide variety of fillers have been tried in this preliminary program, including Silene EE, Ti O_2 (Rutile) du Pont 510, Silica 1240, Celite 505, Dicalite PS, Dicalite white, Dicalite #1, Mapico red 297, Lithopone, Fume Silica, $CaCO_3$, Hi Sil and Linde Silica.

Milling.

In most of the compounding the following technique in milling has been used. The gum broken down on cold rolls set as tightly as possible. Filler is added after the gum is broken down and finally benzoyl peroxide is put in. Milling is continued until a small ball of stock could be formed in the fingers without

showing laminations.

Variations of this technique have been tried such as using rolls at higher temperature and changing the order of adding ingredients in the milling process but the data are not sufficiently numerous to justify drawing definite conclusions yet. Further work on this point is in progress.

Curing.

Compounds are press cured at 220°F for 15 minutes. The mold is then put in the press at room temperature and cooled to room temperature before removal. Two final cure cycles have been used. The first and simplest (Cycle A) is at 300°F overnight. The second (Cycle B) cure cycle is described in detail in section V page 24 . The latter final cure is now standard on all batches. This particular curing cycle has been developed by the staff of Connecticut Hard Rubber Co. as the most satisfactory for general curing of silicone rubbers.

Results.

A detailed account of batches compounded so far is reserved for a later report when enough data are available to justify detailed conclusions. An example will serve to give an idea of the sort of results that are being obtained currently. Using 100 parts by weight of G.E. silicone gum 9979G, 75 parts Ti O_2 and 100 parts Celite 505, the following test results were obtained on 3 successive batches

Tensile	Elongation	Hardness
486	100	70
475	100	67
450	87.5	68

In section IV a detailed outline of the program for the immediate future is given.

V. EQUIPMENT

Apparatus for High Vacuum Treatment of Pigments

Apparatus Description

The pigments are thoroughly cleaned by subjecting them to a temperature of about 1000°C and a pressure of 10^{-4} mm Hg or lower. The apparatus for this treatment is shown schematically in figure 1.

The pigment to be treated is placed in a quartz or Vicor (96% SiO_2, Corning Glass Co) boat and inserted into the 1 inch I.D. quartz tube Q. Stopcock S-5 is so arranged to allow insertion or removal of the boat when the plug is removed. F is a hinged-type combustion tube furnace (maximum safe working temperature 1000°C, length 18", made by Hevi Duty Electric Company, Milwaukee, Wisconsin).

The remaining equipment below and to the right of the furnace is for maintaining a high vacuum in the quartz tube. The light-lined sections are of Pyrex glass except for the 30 inch quartz section going through the furnace. The Pyrex quartz tubes are joined together by graded seals. Metal sections on the diagram are shown with dark lines.

The roughing or fore-pump P is a Welsh Two Stage Duo-Seal Pump No. 1397, free air capacity 5 liters/sec. with a pumping speed of about 2 1/2 liters/sec at 10^{-3}mm Hg. (manufactured by W.M. Welch Scientific Co., Chicago, Illinois). The high vacuum oil diffusion pump D is a VMF 50 W, with an ultimate vacuum of 10^{-6}mm Hg and a pumping speed of 50 liters/sec at 5×10^{-4} mm Hg. (manufactured by Distillation Products Inc., Rochester, N.Y.)

T-1, T-2 and T-3 are cold traps to freeze out all desorbed vapors before they can reach and contaminate the pumps. These traps are cooled with the conventional dry ice, chlorofrom, and carbon tetrachloride mixture to a temperature of -78°C.

V-1 and V-2 are vacuum pressure guages V-1 is a thermocouple guage (Type 501, National Research Corp., Cambridge, Mass), sensitive between 1 mm Hg and 10^{-3}mm Hg. V-2 is an ionization guage (Type VG-2, Distillation Products Co., Rochester, N.Y.), usable below 10^{-3}mm Hg. Circuit diagrams of the electronic measuring equipment used with each of these guages is shown in figures 2 and 3.

R-1 and R-2 are rubber tube sections for flexibility and convenience of assembly. Likewise, the metal sections U and V contain sylphon bellows for flexibility and reduce the chances of glass fracture due to vibration, thermal expansion, or accidental jarring of the apparatus. The bellows are in the symmetrical U tube arrangement so that no strain on the apparatus will occur when the bellows contract or expand as the pressure in the system is charged. These metal sections are connected to the glass tubes by glass-Kovar metal seals (Kovar and Kovar-Pyrex glass seals are obtained from Stupekoff Ceramic Co., Latrobe, Penn).

A soft-solder cup joint C-1 allows the diffusion pump to be decoupled easily from the vacuum system for cleaning and another soft-solder cup joint C-2, together with a ground glass ball joint J, allows the quartz tube section containing the pigment to be removed easily when required. Since stopcocks S-4 and S-5 allow the quartz section to be sealed off under high vacuum, it is thus possible to weigh this section before and after evacuation of a pigment and obtain the loss of weight in the cleaning process. It is also possible to remove the boat containing the pigment through stopcock S-5 for weighing if one is not concerned about adsorbed gases on exposure to air.

The glass stopcocks are of the Hg seal type, carefully ground to be tight under high vacuum conditions. These cocks and most of the other high-vacuum glass apparatus were fabricated by F. Pierce Noble, Hamden Conn.

Typical Operation

To illustrate the use of the system, a typical pigment cleanup treatment would run as follows: after weighing the pigment it is inserted in the boat 13 in place in the quartz tube Q. With stopcock S-7 and S-8 open and s-6 closed the forepump P and the furnace F are turned on. Thus the preliminary clean-up is performed by the fore pump above without aid of the diffusion pump, D. Trap T-2 can be used with water ice and T-3 with dry ice if the amount of water in the system is sufficiently large to make clogging the traps possible. Thus the water would be taken out only by the trap T-3 avoiding clogging trap T-2 which collects the higher boiling vapors. A large well in the bottom of these traps allows for considerable

contamination before removal or cleaning of the trap is necessary.

When the pressure has reached 10^{-1} mm Hg or lower the diffusion pump D is turned on, stopcock S-7 is closed and S-6 opened to the cold trap T-1, diffusion pump D and fan pump F. With this arrangement the pressure can then be lowered to 10^{-4} mm and lower.

At the end of a run, when the quartz tube has cooled, the boat is removed and weighed thus establishing the loss in weight of the pigment.

This equipment has been used successfully so far to clean up batches of Celite 505, TiO_2 (Rutile) du Pont 510, and Innis Speiden Silica 1240.

Coating of the Pigments

One of the procedures planned in the general program is to coat the pigments with a silicone film by hydrolysis of dimethyl silicon dichloride on the surface of the pigment. The apparatus to the left of the furnace in figure 1 is designed for this purpose. After treating the pigment by heating to 1000°C at 10^{-4} mm Hg for several hours, stopcock S-5 can be closed and S-4 and S-2 opened to a glass flask containing a salt solution for preconditioning the pigment with water vapor. After several hours of pre-conditioning the stopcock S-2 can be closed and S-3 opened to a flask of dimethyl silicon dichloride. In each case the pressure of the system will assume the value of the vapor pressure of the salt and dimethyl silicon dichloride respectively. It is possible to carry on similar pigment treatments with only slight modifications of this apparatus.

Equipment for Compounding and Testing.

1. Thropp 6" x 12" laboratory mill with scraper blade - steam-heated; water-cooled. Front roll 16 1/2 r.p.m.; ratio 1:1.4.
2. Elmes 8" x 8" laboratory hydraulic press, hand-operated. Electrically heated, Partelow controls. Water cooled.
3. Molds for ASTM D15-41.

   2" x 6" x 0.075"

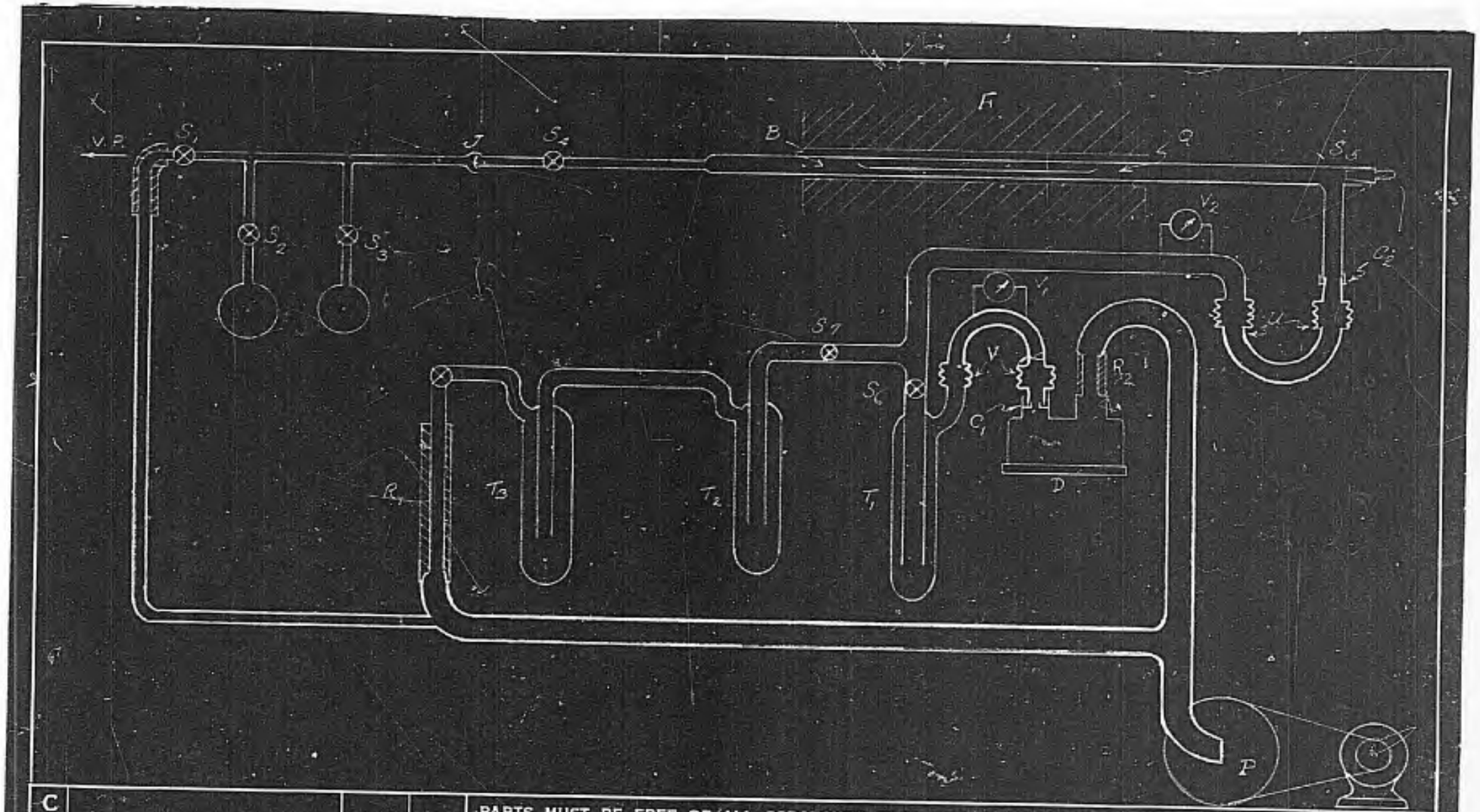
   6" x 6" x 0.075".
4. Dumbbell dies (A and B) for ASTM D412-41
5. Scott tensile tester, model L.P. for ASTM D412-41
6. Shore "A" durometer for ASTM D676 - 47T
7. Laboratory ovens.

   2 Conco-De Khotinsky, Model 95100, 35°C. - 210°C.

   1 Precision model 1240 circulating oven, 35°C - 260°C.
8. Curing oven.

   Electrically heated, circulating, Wheelco Capacitrol set for following following cycle:

Time, hours	Temperature, °F	Time, hours	Temperature, °F
0	70	22	300
1	145	24	325
2	165	26	345
4	180	28	370
6	200	30	390
8-16	225	32	400
18	245	34-42	410
20	265		



LET.	CHANGE RECORD	DATE	BY
C			
B			
A			

PARTS MUST BE FREE OF ALL SCRATCHES, TOOL MARKS, NICKS, AND BURRS. READ NOTES CAREFULLY.

LIMITS ON MACHINE DIMENSIONS UNLESS OTHERWISE SPECIFIED:
ANGLES ± 1/2°
FRACTIONS ± 1/64"
2 PT. DECIMALS ± .010"
3 PT. DECIMALS ± .003"

FINISH

HEAT TREAT

MAT.

SPEC.

SUPERSEDES:

SCALE: Approx 1" = 8" | DWG. SIZE A

DRAFTSMAN	CHECKER	ENGINEER	MOD. OR ORDER NO.	NEXT ASSY.

CUSTOMER PART NO.

ROUGH WGT.
FIN. WGT.

THE CONNECTICUT HARD RUBBER COMPANY,
407 EAST STREET,
NEW HAVEN 9, CONN., U.S.A.

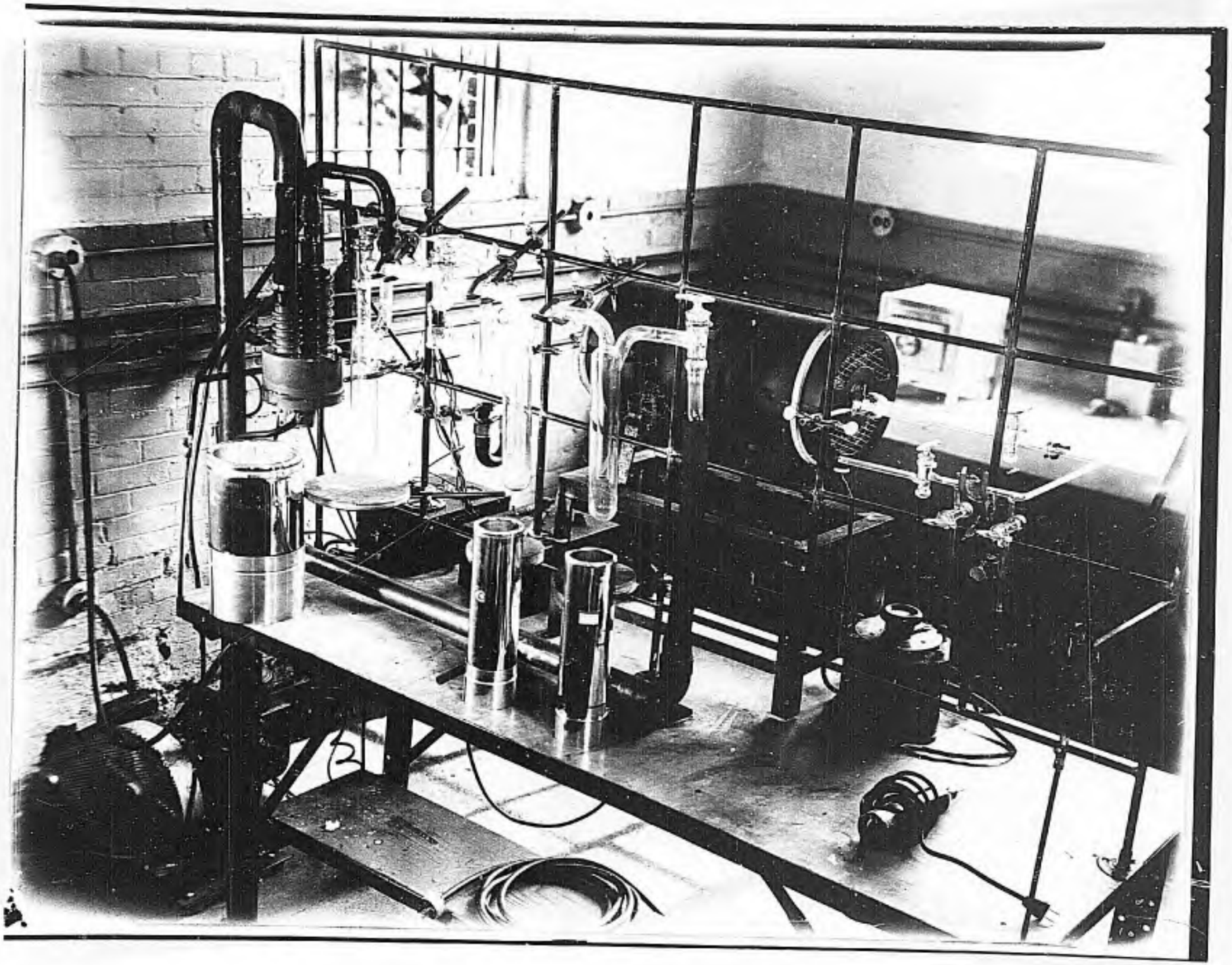
NAME: HIGH VACUUM SYSTEM

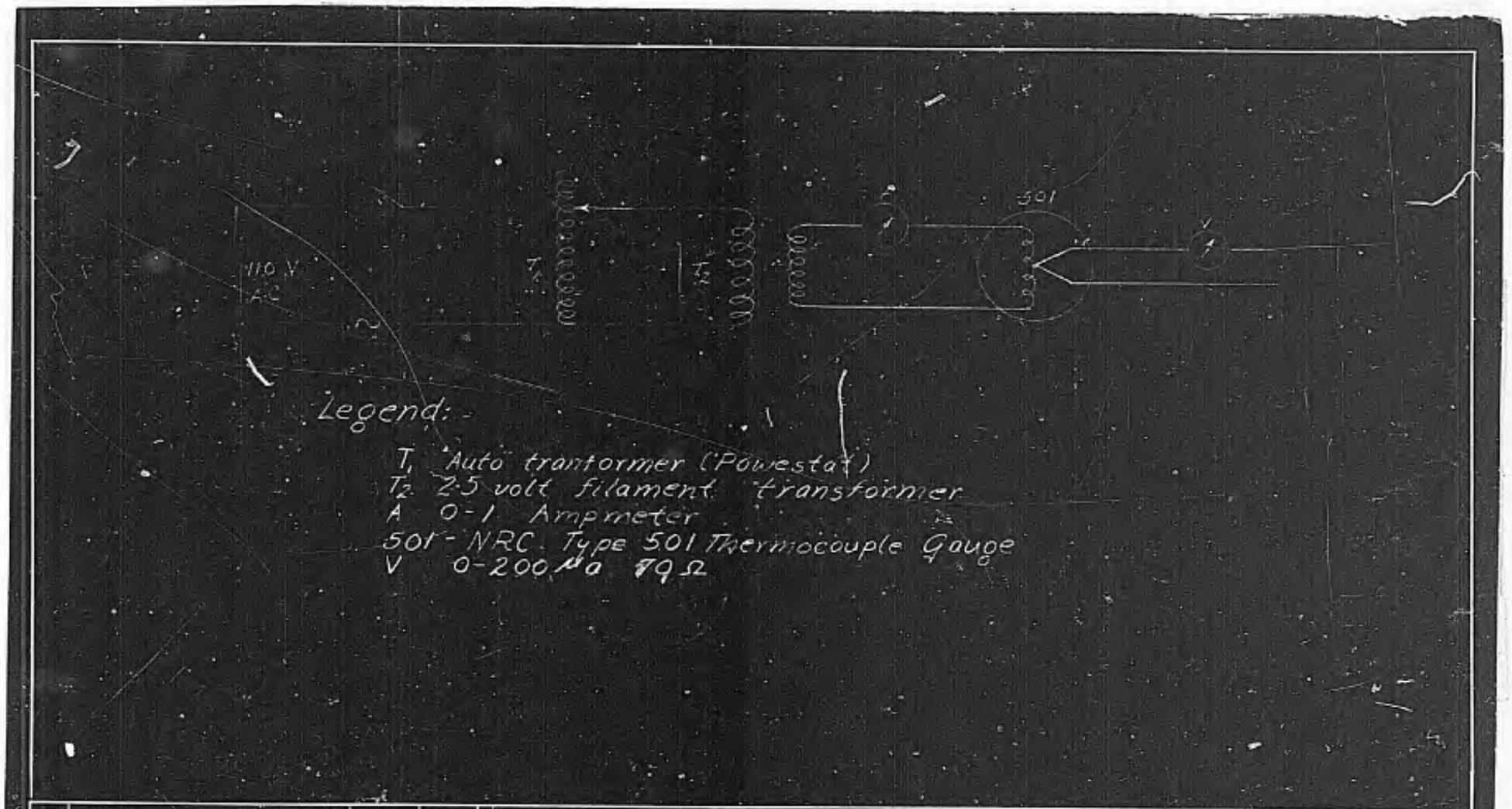
DO NOT SCALE DRAWING
FIGURE 1

PART NUMBER

FORM CHRC-1—2M—8-44

Plate I Photograph of the High Vacuum System for treating pigments at 1000°C and 10^{-4}mm Hg pressure. The tubular furnace is in the center, back of the iron supporting grill. The fore pump is on the floor at the far left.





Legend:

T_1 Auto tranformer (Powestat)
T_2 2.5 volt filament transformer
A 0-1 Ampmeter
501 - NRC Type 501 Thermocouple Gauge
V 0-200 Ma 79 Ω

LET.	CHANGE RECORD	DATE	BY
C			
B			
A			

PARTS MUST BE FREE OF ALL SCRATCHES, TOOL MARKS, NICKS, AND BURRS. READ NOTES CAREFULLY.

LIMITS ON MACHINE DIMENSIONS UNLESS OTHERWISE SPECIFIED:
ANGLES ± 1/2°
FRACTIONS ± 1/64"
2 PT. DECIMALS ± .010"
3 PT. DECIMALS ± .003"

FINISH

HEAT TREAT

MAT.

SPEC.

SUPERSEDES:

SCALE: DWG. SIZE A

CUSTOMER PART NO.

ROUGH WGT.
FIN. WGT.

DRAFTSMAN	CHECKER	ENGINEER	MOD. OR ORDER NO.	NEXT ASSY.

THE CONNECTICUT HARD RUBBER COMPANY,
407 EAST STREET,
NEW HAVEN 9, CONN., U.S.A.

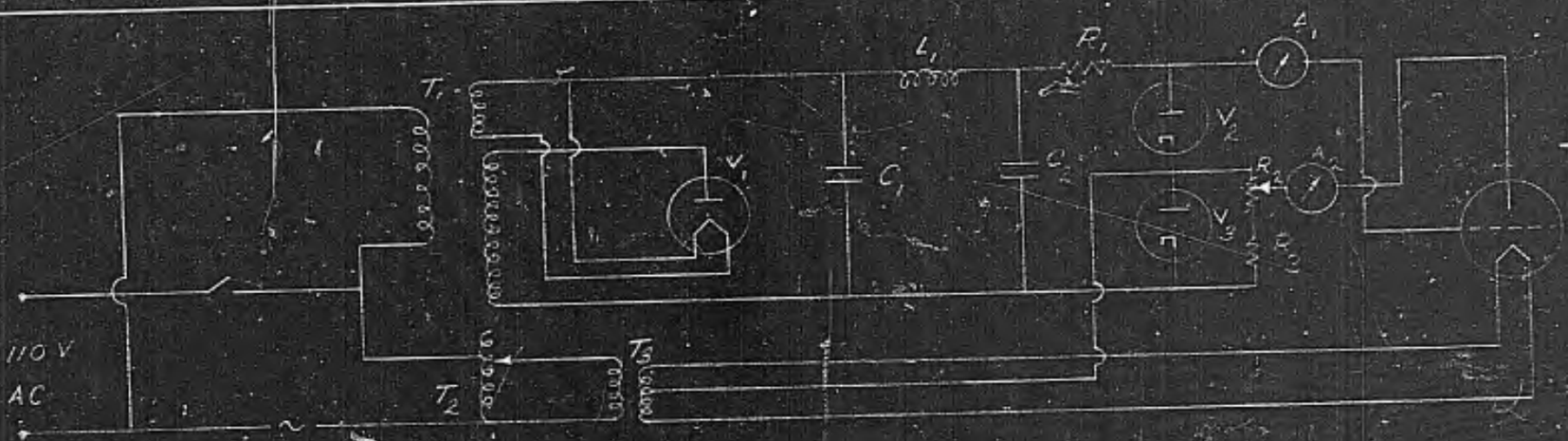
THERMOCOUPLE VACUUM GAUGE CIRCUIT
NAME

DO NOT SCALE DRAWING

FIG. 2
PART NUMBER

FORM CHRC-1—2M—8-44

"ALBANENE" NO. 1995 L. A. & CO., N.Y.



LEGEND:

T_1 -- Power transformer
T_2 -- Auto-transformer (Powerstat)
T_3 -- 7.5 volt, 3.0 amp filament transformer
V_1 -- 5 Y 3 rectifier
V_2 -- V R 150
V_3 -- V R 75
C_1 -- 15μf condenser
C_2 -- 15μf condenser

L_1 -- 8.5 henry 50 MA choke
R_1 -- 15 K 10 Watt
R_2 -- 10 K potentiometer
R_3 -- 10 K 2 watt
A_1 -- 0-25 MA D. C. meter
A_2 -- 0-50 MA D. C. meter
I -- Ionization Gauge
(DPI VG1 or VG2)

LET.	CHANGE RECORD	DATE	BY
C			
B			
A			

PARTS MUST BE FREE OF ALL SCRATCHES, TOOL MARKS, NICKS, AND BURRS. READ NOTES CAREFULLY.

FINISH

HEAT TREAT

MAT.

SPEC.

SUPERSEDES:

SCALE: DWG. SIZE A

DRAFTSMAN	CHECKER	ENGINEER

CUSTOMER PART NO.

ROUGH WGT. FIN. WGT.

MOD. OR ORDER NO.	NEXT ASSY.

LIMITS ON MACHINE DIMENSIONS UNLESS OTHERWISE SPECIFIED:
ANGLES $\pm 1/2°$
FRACTIONS $\pm 1/64''$
2 PT. DECIMALS $\pm .010''$
3 PT. DECIMALS $\pm .003''$

THE CONNECTICUT HARD RUBBER COMPANY.
407 EAST STREET.
NEW HAVEN 9, CONN., U.S.A.

IONIZATION GAUGE CIRCUIT DIAGRAM
NAME

DO NOT SCALE DRAWING

FIG. 3
PART NUMBER

FORM CHRC-1—2M—8-44

"ALBANENE" NO. 1951 KA & CO., N.Y.

Tests Conducted by:

David A. Pulfrey
Rubber Technologist

[illegible]
Rubber Technician

Report Submitted by:

Brigham J. Humphrey
Project Director

Charles A. Walker
Staff Chemical Engineer

Henry G. Fairbank
Staff Physicist

Approved by:

C. M. Boyde
Vice President

7/15/49

SUPPLEMENTARY

INFORMATION

TAB No. 70-3

1 February 1970

IDENTIFICATION	FORMER STATEMENT	NEW STATEMENT	AUTHORITY
AD-494 885 Connecticut Hard Rubber Co., New Haven. Progress rept. no. 1. 15 Jul 49 Contract W-44-109-QM-2161	DDC users only.	No limitation	USAMC ltr, 19 Jun 69