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NAVY DEPARTMENT

BUREAU OF ENGINEERING

Report on

The Preparation and Properties of Solidified Gasoline (II)

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WASHINGTON, D.C.

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INTRODUCTION

(a) Authorization

1. This problem was authorized by OpNav ltr. Op-14 of 11 November 1935, BuEng. 2nd endorsement EE28(11-11-Ds) of 21 December 1935 and BuAero ltr. Aer-E-46-MN JJ 761 of 22 April 1937.

(b) Statement of Problem

2. The present study is a continuation of the investigation of the preparation and properties of "solidified" gasoline. It was thought desirable to extend the work along lines of perfecting the method of preparation and of cheapening the product; some consideration was also paid the various possibilities for recovering the liquid gasoline from the solidified state.

(c) Known Facts Bearing on the Problem

3. The previous work done on the subject at this laboratory is embodied in NRL Report # P-1346. In that report certain characteristics of a suitable solidified product for storage purposes were enumerated. "The emulsion should be hard and tough enough to stand transport, sufficiently friable to be broken into small pieces for the convenience of handling, and must be non-plastic and non-sticky to a degree that the broken pieces do not tend to agglutinate into a single mass. The emulsion should also be capable of easy de-emulsification at will so that the contained gasoline is available as needed. If the product does not possess such properties when made, it should be susceptible to some processing treatment that will produce them." It was found that emulsions of gasoline in alkali caseinate solutions which were subsequently hardened with some agent such as formaldehyde had properties consonant with the requirements laid down above. In addition, such emulsions were found to possess a high degree of resistivity towards water, permitting storage under that medium, were relatively non-inflammable as compared to liquid gasoline, and exhibited a very low rate of evaporation of the contained hydrocarbon. Such properties, when considered from the standpoint of storage possibilities, confer upon "solidified" gasoline the several advantages listed below:

(a) Increased economy by a minimization of the normal loss through evaporation of 8-10%, and a preservation of the starting efficiency of the original fuel by reducing the loss of the lighter ends commonly experienced on long-time storage.

(b) Decreased fire hazard during transport and storage.

(c) Enhanced safety of stocks in the event of an attack by an enemy.

4. The cost of preparing a satisfactory emulsion was found to be in the neighborhood of 6 cents per gallon. This figure was felt to be somewhat excessive even though it is balanced to some extent by the saving effected in lowered evaporation losses and deterioration of the fuel, and by such inestimable factors as the increased safety of government property in wartime and peace.

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(d) Theoretical Considerations

5. The most expensive ingredient in the emulsifying mixture is casein**. It is obvious, then, that substantially to reduce the cost of preparing "solidified" gasoline the quantity of casein used per gallon of liquid gasoline must be kept as low as possible. Although a dispersion of gasoline in water can be made using as little as 3 grams of casein to 1000 grams of hydrocarbon, it will be noted that the emulsion considered herein contains 4-5 times that amount of the protein. The reason for this is that the mechanical strength of the emulsion, its toughness, and, to a degree its resistivity to water depend largely on the actual percentage of casein present. Hence, there is a limit below which the casein content cannot be reduced and still produce a satisfactory product. This lower limit has been found to be 1.8-2.0% by weight of the gasoline used.

6. Another factor for consideration is the gasoline content of the solidified product. The weight of extraneous material (water and emulsifying agent) must be relatively low in order that the finished material contain enough gasoline to make handling and storage in the solidified form feasible. In view of transportation costs and the requirements of storage space, it is believed that an emulsion containing more than 15% inert material is not practicable. Since the minimum amount of casein is in the neighborhood of 2% of the weight of the gasoline emulsified, the only way to increase to percentage of gasoline in the emulsion is to decrease the quantity of water used. It has been found, however, that it is very difficult to reduce the quantity of water to less than 15% by weight. This is true because of the high viscosity of casein solutions and the rapid stiffening of the emulsion as more and more gasoline is incorporated. The rate of increase in the viscosity of the mixture during emulsification is largely dependent upon the initial viscosity of the aqueous phase. When, for example, the ratio of water to casein is 6:1, the resulting solution is quite viscous at the outset and thickens rapidly until a point is reached where the mixture is so stiff that the blades of the beater fail to engage. When such a ratio of water to dissolved casein is present in the emulsifying mixture it was found impossible to prepare dispersions more concentrated than 60-70% in respect to gasoline content. The problem resolves itself into finding some method of regulating the initial viscosity of the aqueous phase so that the preparation of 85-90% emulsions may be easily accomplished. The procedure finally adopted consisted of suspending the requisite amount of casein in such a quantity of water that the finished emulsion would contain the desired percentage of gasoline, and then adding to the suspension an insufficient quantity of an appropriate solublizing agent to dissolve all the casein used. After emulsification, more of the solubilizing agent was stirred in to effect the complete solution of the remaining casein.

** The price of casein has fluctuated between 10 cents and twenty-five cents per pound in barrel lots for the past five years. At the present time, the trend seems to be towards lower price levels. It currently sells for 13-1/2 cents the pound.

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7. Before recourse was had to this plan, however, efforts were made to control the viscosity of the emulsifying medium by regulating the hydrogen ion concentration of the solution. Casein, being an amphoteric substance, is soluble in both acids and bases. Since this is so, it is evident that there must be some narrow range of hydrogen ion concentration at which the solubility of the substance is at a minimum. This point, known as the "isoelectric", occurs at a pH 4.6, defines not only the point of lowest solubility but also the point of minimum viscosity. Though a suspension of isoelectric casein in water is only slightly less fluid than water itself, there is not enough of the protein in solution to act effectively as an emulsifying agent. If an alkali is added to such a suspension, the casein dissolves and the viscosity curve begins to rise, reaching a maximum at pH 8-9; thereafter, the curve drops again as the hydroxyl ion concentration attains higher values. In the more alkaline solutions hydrolytic degeneration of the casein proceeds rapidly. Therefore, to avoid loss of the emulsifying agent by decomposition, the work was limited to those regions of the viscosity curve between the isolectric point and pH 9. By using alkaline salts instead of the free hydroxides as solubilizing agents it was easy to prepare solutions in the desired pH range. The results of these experiments are discussed elsewhere.

8. Still another factor in the cost of the product is the actual length of time required for the preparation and the processing of the emulsions. The greatest consumption of time occurs during the treatment in a hardening bath. Attempts were accordingly made to reduce to a few hours the several days necessary for proper hardening in a bath. The results of these experiments were not very satisfactory. The direct incorporation of hardening agents generally failed because of the speed of the reaction between the agent selected and the casein. Formaldehyde, and even paraformaldehyde, react with such avidity that it is virtually impossible to stir in an adequate amount of the hardening agent without "breaking" the emulsion. In one case, where triethanolamine was used as the solublizing agent, a very satisfactory product, which "set" in 15-20 minutes after the final mixing, was obtained by stirring in paraformaldehyde. Unfortunately, both triethanolamine and paraformaldehyde are relatively expensive substances, selling for about 25 cents and 35 cents per pound respectively. Hexamethylenetetramine and formaldehyde sodium bisulfite release HCHO when treated with dilute acids; however, the only satisfactory method for obtaining a smooth release of the formaldehyde throughout the emulsion was by steeping in acidulated water. The time necessary for this process is as great as that required for hardening in a formalin bath and possesses no advantage over the latter.

9. In summary, the cost of preparing the emulsion may be decreased by (1) utilizing a minimum quantity of casein; (2) employing the least possible amount of water, and conversely, a greater percentage of gasoline, and (3) by decreasing the time required for the process.

10. But, the considerations of the cost of "solidified" gasoline include more than that of the emulsification process alone; the expense involved in recovering the contained fuel for use as needed is also a factor in the ultimate cost of the material. The gasoline may be separated from the solid matrix by two methods, namely, mechanical crushing and expression, and distillation. The former method was utilized in the French Laboratorie pour les Petroles Charbons et Derives and has been investigated. The merits of the

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procedure have been compared with results obtained by dry and steam distillation of the emulsion.

(e) Narrative of Original Work Done

11. A number of emulsions were made employing casein with various solublizing agents in an effort to regulate the hydrogen ion concentration and initial viscosity of the aqueous phase. The reasons for these experiments have been previously outlined. A study of the possibility of directly incorporating hardening agents in order to avoid the necessity of prolonged processing the emulsion in a formalin bath was also made. The most satisfactory product, a casein-silicate dispersion hardened in an acidulated bath of formaldehyde, was prepared in quantity and stored for six weeks. At the end of that time it was examined and used in experiments designed to determine the most efficacious method for recovering the fuel it contained. The recovered gasoline was tested for gum content to determine if storage in the solidified form had had any deleterious effect.

METHODS

12. All the emulsions were prepared by vigorously agitating the gasoline with an aqueous solution of the emulsifying agent in a modified ice cream freezer of one gallon capacity. The machine was so arranged that the mixing can could be rotated at 100 r.p.m. by a 1/4 HP motor connected through a series of pulleys. The contents of the can were maintained at 50-60° C. during the emulsification in order to take advantage of the reduced viscosity of casein solutions at elevated temperatures. The cover of the can was fitted with close rubber gaskets to minimize loss. Usually, 3000 cc (2100 gms.) of the hydrocarbon were placed in the can and allowed to come to the temperature of the surrounding bath. Meanwhile, a quantity of casein not greater than 2% of the weight of the finished emulsion was dissolved in a predetermined quantity of water containing the requisite amount of the selected solublizing agent. For the latter, sodium borate, phosphate, carbonate, bicarbonate, silicate and calcium hydroxides were variously used. Of these, sodium silicate was the most satisfactory. The mixture was then added to the warm gasoline and the beaters started. Emulsification was complete in 10-25 minutes depending on the composition of the water-casein solution. If the product was to be hardened by direct incorporation of a hardening agent, a calculated amount of the chosen material (formaldehyde, paraformaldehyde, hexamethylenetetramine, or formaldehyde sodium bisulfite) was stirred in as rapidly as possible. It was found, however, that the mixture hardened so quickly that a homogeneous blending of the emulsion and the hardening agent could not be accomplished. Usually, therefore, the emulsion was poured into a vat to a depth of about 2 inches and an aqueous solution of the hardening agent poured on top; successive layers of emulsion and hardening fluid were then added until the vat was full. A cover was placed on the container and its contents were undisturbed for 72 hours. The composition of the hardening bath was as indicated: To an amount of water equal to 10% of the total emulsion, 40% formalin was added in the ratio of o.4 part of formaldehyde solution to each part of casein used. This solution was then acidulated with sulfuric acid in a quantity sufficient to reduce the hydroxyl ion concentration to a value corresponding to pH 6. After 72 hours, the solidified product was removed from the container, broken into small bits, allowed to drain somewhat, and was examined. Of the emulsions so prepared, the

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casein-silicate compositions were the most promising. Three gallons of the most satisfactory of this type were made up so that the gasoline content of the finished material was 86% (about 89% on a volume basis) and was stored in a loosely covered contained for six weeks. At the same time a small quantity was placed under water and allowed to remain for the same period to check on its water stability. At the end of the six-week's storage, the emulsion was examined and then used in tests to determine the best method for removing the contained gasoline.

13. The machine* which had been received from France in connection with this work was first tested. The apparatus consisted essentially of two revolving rollers into which the granules of solidified gasoline could be fed by a hopper-like arrangement and between which they could be crushed and the liquid portion expressed. The machine was so designed that the solid matter would be extruded between the rollers and out the back of the apparatus and would act as a seal to prevent any liquid gasoline from escaping by the same route. The freed gasoline was supposed to run over the rollers, drip down them into a collecting pan from which it could be led off through a pipe. The device was tested not only with the solidified gasoline made at this laboratory but also with samples of that obtained from France. In no case was the operation satisfactory; nor did the results obtained here check with the success claimed by the French inventor with its use.

14. Neither could satisfactory yields of gasoline be obtained by pressure filtering. When the pulverized product in a filter cloth was placed in a press and pressure applied, a small amount of freed gasoline was collected. Soon, however, the solid matrix so filled the meshes and interstices of the cloth that no more liquid could be made to pass.

15. Recourse was then had to distillation methods. Weighed quantities of the emulsion were placed in flasks equipped with efficient condensers and the gasoline was expelled either by direct heating or by steam stripping. Dry heat was found to cause considerable pyrolytic decomposition of the casein with an accompanying contamination of the distilled gasoline by ill smelling products which could not be removed with a caustic wash. The charred organic matter inevitably fouled the bottom of the still pot, was difficult to remove, and reduced the efficiency of heat transfer to the contents of the pot. In light of these facts, steam distillation is to be preferred. It was found that steam, heated to 150° C. caused the complete removal of the gasoline from the solid matter. The process was accompanied by no frothing, and at the end there was left in the still pot a yellowish, somewhat damp, pulverulent, easily removed residue. For the stripping of the gasoline from 1000 grams of the 86% emulsion, under the conditions of the laboratory experiment, 525 grams of the superheated steam were required. The distilled gasoline was given a caustic wash to remove the yellow tint and the odor acquired during the distillation. This product was then tested for gum by the ASTM Method No. D381-34T; the gum content was about the same or slightly less than the original gasoline.

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* Drawings of the device are found in Appendix A.

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DATA OBTAINED

TABLE I

The Composition and Characteristics of
NRL Casein-Silicate Emulsion

Composition

Total Solids		2.6%
Casein	1.83%	
Na_2SiO_3 (dry)	0.77	
Water		11.4
Gasoline		86.0
		100.0%

Details of Preparation:

3000 cc (700 gm) of gasoline were placed in the emulsifier, the temperature brought to 50° C., and a mixture of 45 gms. of casein in 250 cc of water containing 3 cc of 40% sodium silicate solution was added. The beaters were started and the emulsification was completed in 15 minutes. The can was then opened, 33 cc of 40% silicate was added and the stirring continued for 5 minutes longer. Thereupon, the emulsion was transferred to a small vat and stratified in layers approximately 1.5 inches thick which were separated by thin layers of the hardening agent. A total volume of 300 cc of an aqueous solution of the hardening agent containing 18 cc of 40% formalin and 5 cc concentrated sulfuric acid. The volumes of this solution applied between the layers of emulsion were roughly equal. After hardening 72 hours, the product was removed from the vat, allowed to drain, and was placed in storage.

Characteristics

(1) Appearance: white and somewhat translucent; on aging for 6 weeks the solid acquired a definite yellowish tint and became very noticeably translucent.

(2) Water Stability: Unaffected by storage under water for six weeks.

(3) Strength: Sufficiently strong and tough to withstand ordinary handling.

(4) Flammability: The emulsion will ignite if held directly in a flame. The combustion is not very vigorous and the flame may be easily extinguished by the application of water. When the surface of the solid has been previously wetted, it is practically non-inflammable.

(5) Efficiency in minimizing gasoline evaporation: It is as efficient as the French emulsion (see report NRL P-1346, pages 4 and 6). The solidified gasoline has an evaporation rate of about 1/5 that of liquid gasoline of the same type.

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TABLE II

Comparison of the Various Methods of Recovering the Gasoline

Method	Quantity of gasoline recovered from 200 gms.	
	From French Emulsion	From 86% NRL Emulsion
Mechanical separation with the apparatus from France	51 gms.; 25.5% (a)	109 gms.; 54.5% (b)
Dry Distillation	158 gms.; 79% (a)	168 gms.; 84.3% (b)
Steam Distillation	---- ----	170.3 gms.;85.1% (c)

(a) Average of two runs.
(b) Average of three runs.
(c) Average of 5 runs calculated from the data given in Table III for 1000 gm. samples.

TABLE III

Recovery by the Method of Steam Stripping

Run	Weight Gasoline from 1000 gms.	Weight Water Collected*	Weight Steam Required*
1	845 gms.	629 gms.	515 gms.
2	848	641	527
3	859	650	536
4	852	641	527
5	851	634	520
average	851	---	525

* The emulsion contained 11.4% water, which must be deducted from the total volume of the water in the condensate in order to find the actual amount of steam required.

Gum Content of Gasoline:

Distilled from Emulsion	Original
0.5 mg./100 cc	0.9 mg./100cc

[redacted]

CONCLUSIONS AND RECOMMENDATIONS

(a) Facts Established

(1) Bearing on the problem.

16. Gasoline can be emulsified with an aqueous casein-silicate solution which may then be hardened with formaldehyde to yield a substance of the appearance and consistency of art gum. This material has been designated as "solid gasoline" and has interesting possibilities from the standpoint of the storage of gasoline stocks. It is relatively non-inflammable, is water resistant, hard and tough enough to stand moderately rough handling, and exhibits a very low rate of evaporation for the contained gasoline. Its preparation is attended with no especial difficulties, and from it liquid gasoline can be recovered easily and unaltered by steam distillation. The cost of the materials used in the preparation of the emulsion is about 2 cents per gallon. The expense of the gasoline recovery is estimated at 30 - 50% of that figure. This estimate is qualified by the remarks contained in Appendix A.

(2) Collateral Facts.

17. The study made of the apparatus received from France which was designed to recover the gasoline by a mechanical separation from the solid matrix demonstrated that the machine performs poorly the function for which it was intended. The claims of the inventor could not be substantiated either by the use of some of his own product or that prepared at the Naval Research Laboratory. Experiments have indicated that the most satisfactory method of recovery entails a stripping of the emulsion with super-heated steam. It will be noted (Appendix A) that the expense of recovery of the gasoline from the emulsion is figured on a theoretical basis of BTU per gallon rather than in terms of actual cost and that an estimation of power and labor cost has been neglected. It is very difficult, on the basis of a very small scale laboratory production, to give a reliable estimate as to what these factors will be. The indications are, however, that they will be low and should be within the range of o.5 - 1.0 cent per gallon.

(b) Opinions

18. It is believed that gasoline can be solidified and recovered for use at a maximum cost of about 3 cents per gallon -- all factors considered. At this figure it is felt that the storage of gasoline in the emulsified form is feasible in climates where high prevailing temperatures occasion considerable fuel loss and impairment through volatization. Its use in depots where the fire hazard is great is also indicated. Since the material may be stored under water and may thus be rendered practically bomb-proof, the advisability of stocking gasoline in the solid state in sections liable to attack by an enemy is evident.

(c) Recommendations

19. A quantity of solidified gasoline is being prepared and stored under conditions common to Naval practice; after a suitable period

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it will be examined and subjected to test to determine if the material is as useful in actual practice as it seems to be from laboratory experience.

SUMMARY

20. An improved method has been worked out for the preparation of "solidified" gasoline, and its cost of production has been lowered to the neighborhood of 2.0 cents per gallon.

21. Methods for recovery of the emulsified gasoline have been studied. Stripping with super-heated steam seems to be the best procedure.

22. The total cost, inclusive of materials, expense of recovery, labor, and power, is tentatively estimated at about 3 cents per gallon.

[redacted]

APPENDIX A

The cost of recovering gasoline from the emulsion will vary with the locality where the operation is performed and will depend upon prevailing labor cost, the availability of the requisite energy, and the efficiency of the equipment employed. Hence, it is not feasible to translate the present laboratory results to the basis of plant operation. No attempt will be made to predict accurately the requirements for labor and equipment. However, the theoretical amount of energy necessary for recovering the fuel can be figured and is submitted in terms of BTU per gallon rather than in actual cost. As a matter of interest, the BTU requirement per gallon of recovered gasoline as found by laboratory experiment is also given. It is understood that the results obtained are illustrative only of a very special case and are not to be taken as criteria for the operation of plant equipment. Large scale operation with properly designed equipment will doubtlessly be more efficient.

Although the considerations of equipment cost, labor and power, figure also in the expense of preparing the product, here the predominant factor is the price of the materials used. Accordingly, the preparative costs are given in terms of the current prices of the chemicals employed with the understanding that due allowance must be made for the other factors. These data are given in Table IV.

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TABLE IV

Costs of Emulsification and Recovery of Gasoline

(Based on 1000 cc of gasoline)

Preparative Costs

15 grams casein at 13-1/2 cents per lb.	0.447	cents
15.7 grams Na_2SiO_3 at 8 cents per lb.	0.028	"
6.0 grams formalin at 5-3/4 cents per lb.	0.077	"
3.0 grams H_2SO_4 at 3/4 cents per lb.	0.005	
Cost per liter	0.557	Cents

Since one gallon contains 3.78 liters, the cost per gallon is.. 2.11 cents

Recovery Costs in BTU per Gallon

(1) Theoretical

The three components of solidified gasoline (gasoline, water, casein-silicate) are to be heated from an initial temperature of say, 80° F. to 212° F. and the water and gasoline are to be evaporated with superheated steam. The amount of heat so required will be the sum of the specific heats per degree of the three components times the number of degrees of temperature change, plus the latent heat of evaporation of water and gasoline. One pound of Naval Research Laboratory 86% emulsion has the following composition:

Water = .114 pounds
Gasoline = .860 "
Casein-silicate = .026 "

and $H_{latent(H_2O)}$ = 970 BTU per pound
$H_{latent(gasoline)}$ = 131 BTU per pound
$Sp.H_{(gasoline)}$ = 0.54 BTU per degree
$Sp.H_{(casein\text{-}silicate)}$ = 0.4 BTU per degree (assumed).

Therefore the heat requirements for each component are:

.114 x (212 - 80) = 15.05 BTU
.114 x 970 = 110.58
125.63 BTU for water (A)

.86 x (212 - 80) x .054 = 61.30 BTU
.86 x 131 = 112.66
173.96 BTU for gasoline (B)

.026 x (212 - 80) x 0.4 = 1.37 BTU for casein-silicate (C)

(A) + (B) + (C) = 300.9 BTU per pound of solid gasoline.

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TABLE IV (CONT.)

One gallon of the gasoline used weighs 5.83 pounds and comprises 86% of the finished emulsion. Therefore, one gallon of gasoline (liq.) is the equivalent of 6.78 pounds solid gasoline. Hence one gallon of gasoline (liq.) requires 6.78 x 300 = 2034 BTUs.

(2) Laboratory Results.

From the data in Table III, the recovery of 1000 cc or 700 grams of gasoline from the 86% emulsion requires -

$$\frac{525 \times 700}{851} \text{ or } 448.0 \text{ grams of steam.}$$

Heat required to raise 448 grams of water from 25° C. to the boiling point, vaporize it, and superheat the vapor to 150° C., is approximately 1197 BTU. From this it follows that 4525 BTU were necessary to remove one gallon of gasoline from the emulsion.

Using 21,000 BTU/pound as the calorific value of gasoline and 5.83 pounds gasoline per gallon, the BTU value of gasoline/gallon is 113,000. Using the above data of 4525 BTU per gallon for recovery, there is a consumption of 4525/113.000 x 100 or 4% of the gasoline for recovery. What the balance will actually be in plant practice is hard to predict.

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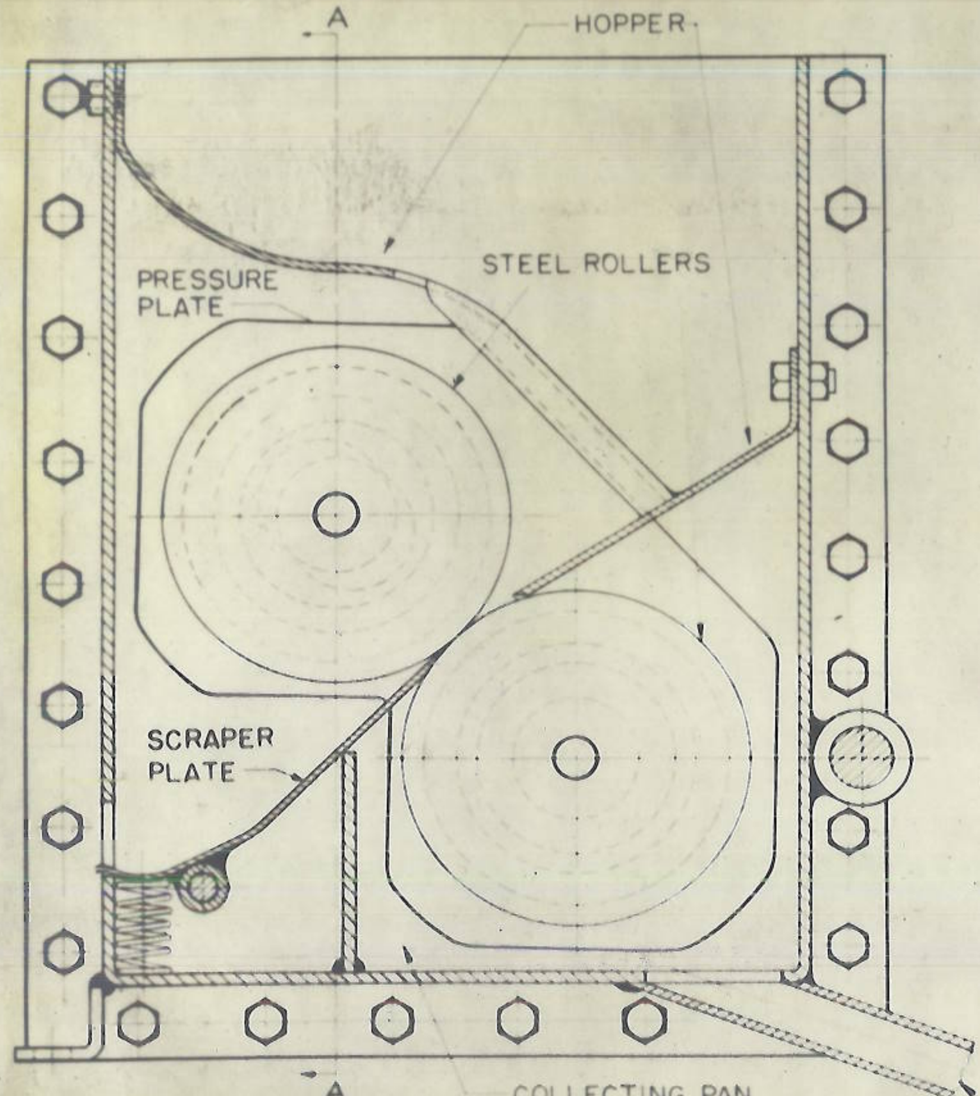
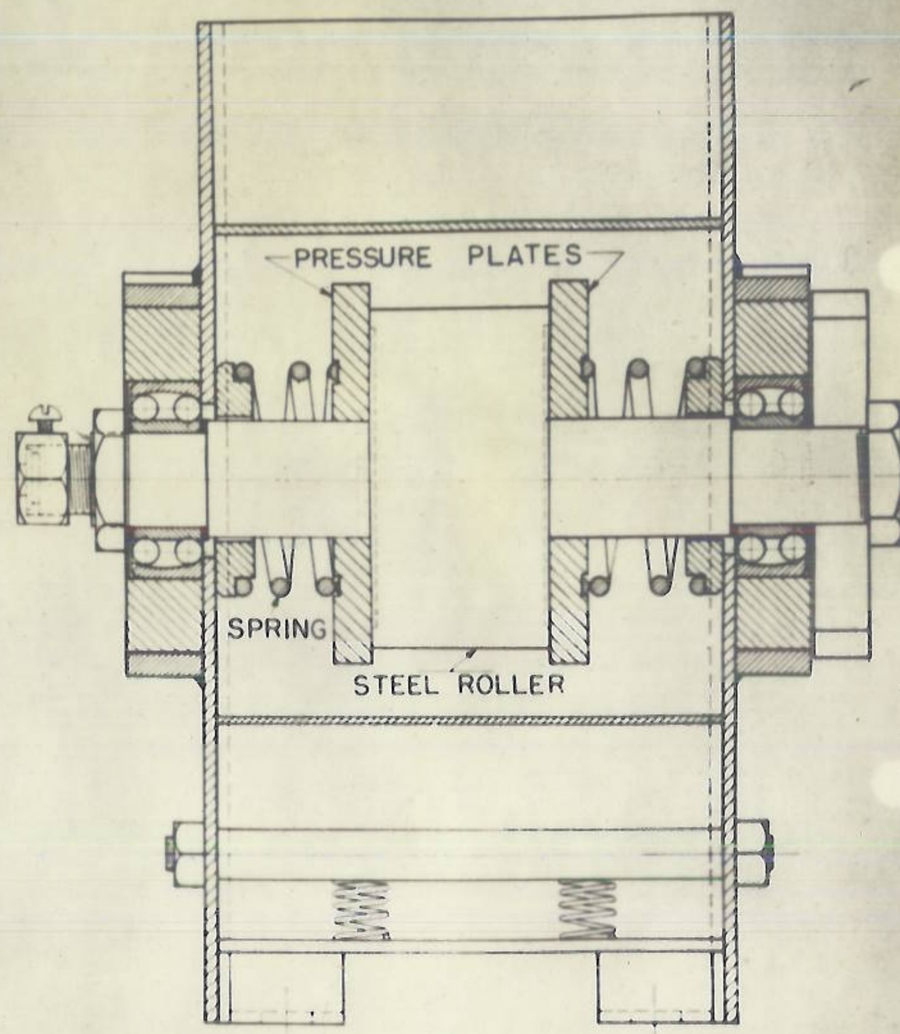


SIDE VIEW
WALL OF HOUSING BOX REMOVED



SECTION A-A