LE 3 B7
1940 A8
C 3 D3

THE DEVELOPMENT OF A PRESERVATIVE
FOR GILL NETS.

by

Ganillo
G. Cave-Browne-Cave

A Thesis submitted for the Degree of
MASTER OF ARTS
in the Department of
Chemistry.

THE UNIVERSITY OF BRITISH COLUMBIA

April, 1940.

*Accepted on behalf of the
Department of Chemistry*

Head of Department of Chemistry

It is with real pleasure that the author acknowledges the helpful criticism and un-failing interest of Dr. R.H. Clark, Head of the Department of Chemistry.

INDEX.

Page No.

1. Causes of net deterioration.....	1
2. Required properties of a preservative....	3
3. Methods of measurement and description of instruments.....	4
4. Effect of solvents on tensile strength of strands.....	11
5. Preparation of chlorinated rubbers.....	12
6. Method of impregnating strands and of immersing strands in sea.....	20
7. Results of sea immersion tests on strands coated with prepared chlorinated rubbers.....	21
8. Extent of knot slippage.....	23
9. Effect of plasticisers in the chlorina- ted rubber film.....	25
10. Effect of time of immersion of strand in impregnating solution.....	33
11. Effect of concentration of Tornosit on the life of the treated strand.....	35
12. Effect of impregnating strand with a toxic salt prior to impregnation of strand with Tornosit.....	38
13. A further study on the use of several commercial plasticisers.....	
14. Variation of flexibility of strand with varying concentrations of plasticiser..	
15. Variation of wearing quality of strand with varying concentration of plasticiser.....	
16. Per cent. increase in weight of strand due to treatment.....	
17. Results obtained on using the preservative under actual fishing conditions.....	
18. Summary.....	
19. Bibliography.....	

The present paper records a somewhat thorough investigation of the use of chlorinated rubber for preserving salmon gill nets.

Fisher and Tyner (o) have attempted to use various plastic preservatives. Their work showed that, of all the plastics they tried, chlorinated rubber offered the greatest promise.

The More Important Causes of Net Destruction.

Mechanical wear of a net is of prime importance, in that if an effective net preservative is found, mechanical wear will probably be the dominant factor determining the life of the net. Wear results from the threads rubbing against one another, against boat gunwales, floats and leads. Moreover, tears from snagging effect materially the life of a net.

Bacterial action appears to be the dominant cause of nets rotting in the sea. Fleming and Thaysen (1) in their work on the deterioration of cotton when stored, showed that (a) exposure to damp renders cotton brittle and short-fibred, (b) cotton on wet storage does not deteriorate in absence of micro-organisms, bacteria therefore being responsible for the breakdown. These experimenters chose a cotton waste sample with a bacterial count of 10^6 per gram. This, on wetting, showed, by microscopic examination, extensive damage after five days. A carefully hand-picked cotton sample, taken from balls with a bacterial count of 20,000 per gram, when wetted could be left damp for twenty days before fibres were visibly attacked.

2.

Dorée (2), in an interesting set of experiments, showed that if bacterial action is prevented, rotting of cotton line is essentially prevented. While bacteria act on cotton in absence of oxygen, the presence of oxygen results in greater damage to a cotton line by bacteria. Moreover, with oxygen and bacteria present, microscopic examination of a cotton line exposed to these showed cuticular damage to fibres, due solely to the cellulose decomposing shizomycete, streptothrix not being found.

Robertson (3), showed that when the tensile strength of a fishing strand began to decrease, during sea immersion, bacteria had simultaneously entered the lumen of the fibre (cotton). The fibres began to swell rapidly after this entry. There occurred, coincidentally, a rapid growth of bacteria, probably feeding on the nitrogenous matter of the pith. The fibres during the growth of bacteria gradually wasted away. Robertson also points out that slime from fish-nets is very rich in cellulose-attacking bacteria; and that species of hydra, in particular the red variety, in settling on nets, may in themselves be harmless, but owe their destructive properties to the fact that they constitute a good place for bacterial growth.

The fact that toxic salts, e.g., copper sulphate, and copper naphthenates, are effective gill net preservatives, lends support to the theory that bacterial action causes the most extensive deterioration of nets.

is
Sunlight/by some considered a cause of deterioration (Q). Its importance, relative to bacterial action, is difficult to estimate. Waentig (4) exposed cotton fibres to direct illumination from a mercury vapour arc for twenty-four hours. The strength of the fibres was thereby reduced by over 50 per cent. Barr and Hatfield (5), found sunlight to be without effect on cotton in a hydrogen atmosphere. Oxygen caused considerable deterioration, which effect was accelerated by moisture, acids and iron.

Oxidizing agents undoubtedly contribute to the deterioration of nets. Again the relative importance of oxidation is difficult to estimate. The experiments of Esselen (6), and Tiltman and Porritt (7), indicate oxidation of cotton occurs to a considerable extent at temperatures of approximately 100 degrees Centigrade. Pakschewr (8), showed ultra-violet light accelerated the formation of oxycellulose. Certain metals, e.g., Cu, act catalytically.

Required Properties of a Preservative.

The above discussion on causes of net destruction is admittedly brief. Its sole purpose was to indicate some of the properties a preservative should possess. Such properties, gleaned from the above discussion, may be enumerated.

1. Resistance to mechanical wear. This can, as we shall see later, be partially achieved by using a chlorinated rubber coating around the fibres of the strands of which the net is made.

2. Prevention of bacterial action. Since it is most improbable that a plastic film is toxic, prevention of bacterial action on strands can only be accomplished, obviously, by preventing the bacteria coming into contact with the strands. To achieve this it would be necessary to coat the fibres of the strand with a plastic film impermeable to bacteria. Such a film must be permeable to water; however, since a wet strand has 50 per cent. greater tensile strength than a dry strand, a film impermeable to water would, therefore, give to the strand the very undesirable property of low tensile strength.

3. Prevention of oxidation of cellulose. In addition to these required properties, we must add four more:

(1) Required degree of flexibility. It is essential that nets have the desired degree of flexibility. This property presents a distinct problem when attempting

4.

to use plastic films as preservatives. Some plastic films used by Fisher and Tyner (Q) may have had possibilities, had not lack of flexibility eliminated them at once.

(2) Absence of knot slippage.

(3) Small weight increase. While considerable importance is usually attached to the per cent. increase in weight of a strand due to preservative, two factors will reduce this importance. First, mechanical methods are coming into use for hauling in nets. Second, in the present investigation a semi-water-proofing agent is used, which due to the buoyant effect it causes the net to have when the net is in the sea, compensates for the per cent. increase in weight which the preservative entails.

(4) Since fishermen often demand different colours for their nets, depending on the waters in which the nets are to be used, it is preferable to have a transparent preservative to which there may be added a dye.

Methods of Measurements,
and Description of Instruments.

5 x 40 white strands, made from Irish linen, were used exclusively in all experiments.

Measurements fall into four classes:

1. Tensile strength.
2. Flexibility.
3. Per cent. weight increase.
4. Wearing quality.

Tensile Strength:- A standard instrument, manufactured by Henry L. Scott and Company, was used exclusively. The drums, around which the strand was wound, were 9 inches apart for all measurements listed below. All strands were broken dry. Those immersed in the sea were allowed to dry for two days in the Laboratory.

Flexibility:- Fisher and Tyner (a) used no apparatus for their flexibility determinations. Taylor and Wells (9) have devised an instrument by means of which a quantitative determination of flexibility may be made. Their method consists in measuring the energy dissipated when the strand bends through a definite angle. One end of the strand is attached to a brass plummet. The other end is held rigid. This, then, constitutes a pendulum. A definite initial phase is specified, and the number of oscillations to reduce the angle of the initial phase to one-half, is taken as a measure of the flexibility. Such a method has obvious disadvantages. These are recorded by Taylor and Wells (9), who correct for the errors. Probably the greatest disadvantage is the large number of measurements which must be averaged in order to obtain a figure of significance.

To enable a significant measure of the flexibility of a strand to be made with as few measurements as possible, a new instrument was devised by us.

Procedures for Flexibility Instrument:- One of several procedures can be used, the choice being dependent on time available and on accuracy required. First is given the procedure worked out and adopted in this investigation.

Select a strand for a preliminary test. Add 10 grams to each scale pan. To one pan select a weight (W_2) necessary to cause the pan to fall approximately 3 centimetres in 25 seconds. Next, select a weight (W_1) necessary to cause the pan to fall approximately 3 centimetres in 10 seconds (W_1 is usually from 2 to 5 grams less than W_2). Finally select a weight (W_3) necessary to cause the pan to fall approximately 3 centimetres in 40 seconds (W_3 is usually from 2 to 5 grams greater than W_2). These

preliminary tests gives the weights W_1 , W_2 , W_3 , to be used in the actual determination. We now describe the actual determination.

Select a new strand, add 10 grams to each pan. To one pan add in addition W_1 grams. (The length of strand chosen must be such that when one pan is near the pulleys (the pan containing W_1), the other pan almost touches the base of the instrument). Keep pans from moving by slight pressure of finger on one pulley. Now release finger, allowing pans to accelerate, and coincidentally start stop-watch. Allow pan to fall exactly 3 centimetres; stop the watch, and coincidentally stop the pans moving by pressing against pulley. Record time for 3 centimetre fall, say t_1 seconds (approximately 10 seconds). Repeat exactly the above procedure, using W_2 grams, instead of W_1 , and again record time for 3 centimetre fall, say t_2 . Repeat exactly the above procedure, using W_3 grams instead of W_2 , and again record the time for a 3 cm. fall, say t_3 seconds. By this time 9 centimetres of strand have been used. We have now got three sets of values, namely (W_1, t_1) , (W_2, t_2) and (W_3, t_3) .

Weight W_3 now rests on the scale pan; replace it with W_1 and repeat exactly the entire procedure of the above paragraph. This gives three times t_1 , t_2 , t_3 for W_1 , W_2 , W_3 , respectively. (These times will be found slightly different from those first recorded).

Keep on repeating the procedure, using new samples of strand, until 10 values (or 20 for greater accuracy) are obtained for each of t_1 , t_2 , t_3 . Now average the 10 values for t_1 , the 10 for t_2 , and the 10 for t_3 . Plot a graph - W against T . From the graph read off the value of W corresponding to t equals 25 seconds. This weight W we arbitrarily define to be the average flexibility of the strand.

Of the other procedures possible with the instrument, we may first note that the method adopted (described above) involves interpolation to get W for t equals 25 seconds. If the preservative in the strand is of such a nature that it may be quite evenly applied, then the variation in flexibility may be so small that only one weight, say W_2 , may be required, and one averaged time t_2 , obtained. This of course (see next page)

6.

preliminary tests gives the weights W_1 , W_2 , W_3 , to be used in the actual determination. We now describe the actual determination.

Select a new strand, add 10 grams to each pan. To one pan add in addition W_1 grams. (The length of strand chosen must be such that when one pan is near the pulleys (the pan containing W_1), the other pan almost touches the BASE of the instrument) Keep pans from moving by slight pressure of finger on one pulley. Now release finger, allowing pans to accelerate, and coincidentally start stop-watch. Allow pan to fall exactly 3 centimetres; stop the watch, and coincidentally stop the pans moving by pressing against pulley. Record time for 3 centimetre fall, say t_1 second (approximately 10 seconds). Repeat exactly the above procedure, using W_2 grams, instead of W_1 , and again record time for 3 centimetre fall, say t_3 . By this time 9 centimetres of strand have been used. We have now got three sets of values, namely (W_1, t_1) , (W_2, t_2) and (W_3, t_3) .

Weight W_3 now rests on the scale pan; replace it with W_1 and repeat exactly the entire procedure of the above paragraph. This gives three times t_1 , t_2 , t_3 for W_1 , W_2 , W_3 , respectively. (These times will be found slightly different from those first recorded).

Keep on repeating the procedure, using new samples of strand, until 10 values (or 20 for greater accuracy) are obtained for each of t_1 , t_2 , t_3 . Now average the 10 values for t_1 , the 10 for t_2 , and the 10 for t_3 . Plot a graph - W against t . From the graph read off the value of W corresponding to t equals 25 seconds. This weight W^1 we arbitrarily define to be the average flexibility of the strand.

Of the other procedures possible with the instrument, we may first note that the method adopted (described above) involves interpolation to get W^1 for t equals 25 seconds. If the preservative in the strand is of such a nature that it may be quite evenly applied, then the variation in flexibility may be so small that only one weight, say W_2 , may be required, and one averaged time t_2 , obtained. This of course

eliminates the more lengthy procedure of interpolation.

To obtain the most accurate value for flexibility, a possible procedure would involve obtaining say five times, t_1, t_2, t_3, t_4, t_5 , corresponding to W_1, W_2, W_3, W_4, W_5 , respectively, and plotting W against t . We can then extrapolate and find that value of W corresponding to t equals ∞ . By using a very fine linen thread, we can easily find the frictional force inherent in the apparatus, and, subtracting it from W , get the final value for flexibility.

The merits of the above apparatus are fairly obvious. A quite large sample is used for measurement. Moreover, a given length of strand is bent only six times. This practically eliminates the error likely to be caused by variation of flexibility with number of times a length is bent.

Measurement of Wearing Quality.

Significance of
Measurements of Tensile Strength.

Following are ten measurements of the tensile strength of dry, untreated strand:--

39.0	30.0
36.0	40.0
37.0	36.0
37.0	31.0
32.0	34.0

Average 35.2 (units equals pounds)

These figures are typical of all measurements made, and illustrate the necessity of not only as large a number of measurements as possible for an average value, but also of having some way of telling how significant the average actually is. Thus, if two differently treated strands gave average tensile strengths of 29.0 lbs. and 26.0 lbs., respectively, does the difference, 3 lbs., represent merely fluctuations in sampling? To answer this, there has been used throughout this investigation the following criterion:

We denote "standard deviation" of a sample by σ , and define σ by the formula:

$$\sigma = \sqrt{\frac{\sum d^2}{N}} \quad \text{--- (1)}$$

where N represents the number of samples used in determination of the mean value of the tensile strength (in this investigation N equals 10); and where d represents the deviation, i.e., the difference between tensile strength of a strand and the mean tensile strength of the N strands (Standard Deviation is sometimes called root mean square error).

Now given two sets of samples, we first compute the standard deviation for each set, using equation (1). This gives σ_1 , and σ_2 .

We next denote "standard error of difference" by σ_D , and define it by equation (2).

$$\sigma_D = \sqrt{\frac{\sigma_1^2}{N_1} + \frac{\sigma_2^2}{N_2}} \quad \text{--- (2)}$$

Now let M_1 be the mean of one set of samples, and M_2 the mean of the other set. Define Δ by equation (3).

$$\Delta = |M_1 - M_2| \quad \text{--- (3)}$$

If $\Delta > 3\sigma_D$, then it is highly unlikely that the difference Δ is due to fluctuations in sampling.

Note: The application of the above criterion should strictly be made if $N \geq 20$. We are compelled for economy of time to use $N=10$. Even so, the above criterion is of value.

When tensile strength measurements are given hereafter, the value of σ is given beside it in all cases where the above criterion was used.

Effect of Solvent

on Tensile Strength of Strand.

Procedure:- Strands were immersed in solvent, in corked test tube, at room temperature, for six hours. Strands were then dried in air of laboratory for two weeks, and tensile strength measurements made.

Table I.

Solvent	Tensile Strength (lbs.)
Benzene	36.8
Ethyl Acetate	35.5
Acetone	37.3
Toluene	36.3
Xylene	33.7
Carbon Tetrachloride	33.3
Control	35.2

Preparation of Chlorinated Rubbers.

Staudinger and his co-workers (10) have secured information showing that rubber is built up of long chains of isoprene units, with the formation of a linear polymeric structure.

On the basis of this structure, a possible mechanism for halogenation of rubber would be, according to Kirchof (11)

13.

A.

Formation of a mixture of A and B will explain the variation in per cent. Cl in the product when mode of preparation varies.

McGavack (12) further elucidated the mechanism of chlorination, using a gasometric method. He found: (1) during early stages of chlorination substitution almost exclusively occurs, (2) when rate of substitution decreases, rate of addition increases, accompanied by a fall in temperature, (3) final product is about 65 per cent. Cl, giving an empirical formula $(\text{C}_{10}\text{H}_{13}\text{Cl}_7)$.

The literature on the preparation of chlorinated rubber is extensive. In general, the preparations consist of "dissolving" a sample of rubber in a solvent such as carbon tetrachloride, passing in chlorine gas for a certain time, and then separating, and in many patents stabilizing, the product. Dyche-Teague (13) oxidizes rubber in air or O_2 at 60 degrees Centigrade, disaggregates in a mill, dissolves, then chlorinates. "Solution" of the rubber in solvent is much facilitated by this preliminary oxidation, and this procedure of preparation of sample of rubber was adopted in this investigation. Several solvents for rubber, prior to chlorination, have been recommended. Staudinger (14) used POCl_3 . Others have used CCl_4 , $\text{C}_2\text{H}_2\text{Cl}_4$, C_2Cl_6 , CHCl_3 (15); polychlorides of benzene (16); McGavack

(12) notes that the chlorinated rubber properties depend on type of solvent used.

Conditions of chlorination of the rubber (in "solution") vary with different workers. Staudinger (14) first chlorinates at room temperature, then finally at an elevated temperature. Twiss and Wilson (17) chlorinate with water present as second phase. The water may contain H_2O_2 , $KMnO_4$, $KClO$, to convert the HCl , formed during chlorination, into Cl_2 . Chlorination under pressure has been advocated (18). Addition of a small amount of free sulphur during chlorination has been used (19) (20).

Several methods for obtaining the solid chlorinated rubber have been put forward. Staudinger (14) distills off most of the solvent, and precipitates the chlorinated rubber with petroleum ether. Twiss and Wilson (19) precipitate their product with alcohol. Spencer (21) runs the chlorinated rubber solution into a chamber containing water and glycerol at 135 to 140 degrees Centigrade. The solvent which vaporizes passes into a condenser and is thus recovered. A high speed propeller disintegrates the solid product in the distilling chamber.

Removal of any free HCl in, and stabilization of, the product has been the subject of extensive research. CaO (23) aniline, toluidine (24) $NaHSO_3$, Na_2SO_3 , $Na_2S_2O_3$ (25). Alkali salts of organic acids (26) KOH , Na_2CO_3 , pyridine (27) have been recommended.

Procedure Used in This Investigation.

The rubber was dissolved in carbon tetrachloride, placed in the chlorinating vessel (Figure 1) and chlorine gas passed in for a definite period of time, and at a definite temperature. During chlorination the solution was stirred continuously. The product was separated from the carbon tetrachloride by steam distillation of the latter. Steam was passed into the flask containing the solid chlorinated rubber for a further half hour, after the solvent had been eliminated. The water in the flask was then replaced by fresh water,

and steam blown through for half an hour. The water in the flask was then tested with litmus. If acid, it was replaced by fresh water and steam again blown through for half an hour and water again tested for acidity. If acid, fresh water put in and steam again blown through. This process was repeated until water in flask was neutral to litmus. In this way a stable product was obtained. The water was then drained off the product, the latter crushed to a powder, the powder washed well with water. (In the case of chlorinated rubbers made from pale crepe, a powder was unattainable). The sample was then placed in water, the flask corked, and left twelve hours. The pH was again taken. This washing was continued in this manner until the pH became constant. (For most samples the final pH greater than 5 and always pH less than 7).

<u>Notation of Product.</u>	<u>Number of Washings.</u>					
	1	2	3	4	5	6
A1	2.6	4.0	5.1	5.6	5.7	
* A2	2.4	9.0	7.5	7.1	6.7	6.4
A3	2.6	3.2	3.6	4.1	4.3	4.3
* A5	2.5	9.0	6.5	5.0	3.8	
A6	3.1	4.2	5.2	6.0	5.4	
B1	2.6	3.5	4.0	5.5	5.5	
B2	3.0	4.0	4.8	5.3	5.6	
D1	3.3	4.2	4.3	5.9	4.9	
D2	2.3	3.3	4.0	4.2	5.0	
E1	3.1	3.8	3.9	5.0	6.0	
E2	4.0	5.7	6.0			
E3	3.5	4.9	6.3			
E4	6.0					

* Washed with dilute NH_4OH , then with water.

Since McGavack (12) has pointed out that the properties of the chlorinated product depend on the grade of rubber used, Gutta Percha, Gum Chicle and Pale Crepe were chlorinated, and three quite different products obtained.

Preparation of Chlorinated Gutta Percha.

200 ml. of 10 per cent. solution of Gutta Percha in carbon tetrachloride were chlorinated at 96 degrees Centigrade (water bath used). The rate at which chlorine gas was bubbled through the solution was regulated as far as possible to a constant rate.

Notation of Sample	Time of Chlorination	Remarks.
A1	0.5 hour	medium brown colour, slightly elastic; not powderable.
A2	2 hours	very light brown colour, inelastic; powderable.
A3	4 hours	like A2.
A5	1 hour	
A6	6 hours	

200 ml. of 10 per cent. Gutta Percha were chlorinated for 4 hours.

Notation of Sample	Temperature of Chlorination	Remarks.
B1	0 degrees C. (ice bath)	very light brown powder. Cl ₂ continued to evolve from solution for at least 4 hours after chlorination stopped.
B2	20 degrees C. for 3 hours, then water bath for 1 hour	Like A3.

Preparation of Chlorinated Gum Chicle.

200 ml. of 10 per cent. solution of gum chicle in carbon tetrachloride were chlorinated at boiling point of solution.

Notation of Sample	Time of Chlorination	Remarks.
D1	1 hour	when gum chicle was dissolved in carbon tetrachloride, a considerable rust colored deposit remained insoluble. It was not separated, but chlorinated with the solution. The chlorinated solution had a dark, red brown deposit which was not separated.
D2	4 hours	

Preparation of Chlorinated Pale Crepe.

Pale crepe is a much purer product than either Gum Chicle or Gutta Percha. It is used (28) by Hercules Powder Co., Inc. of Wilmington, Delaware, U.S.A., in their process for manufacturing Tornesit (trade name for chlorinated rubber).

While Gutta Percha and Gum Chicle give 10 per cent. solutions of low viscosity in carbon tetrachloride without initial treatment, preparation of even a 3 per cent. solution of pale crepe not only gives a somewhat viscous solution, but requires a long time for the attainment of a homogeneous phase. To secure a faster rate of, and a less viscous, solution, the pale crepe was first depolymerized by heating in air at 90 degrees C. for 4 hours. A 3 per cent. solution of this product in carbon tetrachloride was made, using a high speed stirrer to aid in disaggregation of the pale crepe.

A 3 per cent. solution of pale crepe in carbon tetrachloride was chlorinated at 50 degrees C. for first hour, 70 degrees C. for second hour and 85 degrees C. for remaining time. (Foaming prevented chlorination at boiling point of solution during initial stages of chlorination).

Notation of Sample	Time of Chlorination	Remarks.
E1	1 hour	All products were porous, fibrous, white masses.
E2	2 hours	
E3	4 hours	
E4	7 hours	

Impregnation of Strands

With Above Prepared Samples of Chlorinated Rubbers.

(a) Composition of Impregnating solutions:-

benzene	100 ml.
chlorinated rubber sample	20 gms.
dibutyl phthalate	6 ml.

Impregnated strands were labelled with the labels of the chlorinated rubber (or gutta percha or gum chicle) with which they were impregnated, respectively. The labels of the chlorinated rubbers were those assigned above, during the description of preparations of the chlorinated rubbers.

The above solution gave strands of requisite flexibility for the chlorinated gutta percha and gum chicle, but for chlorinated pale crepe there was an insufficient concentration of plasticiser. Accordingly, additional solutions were made, to which were added concentrations of plasticiser which gave strands of same degree of flexibility as those impregnated with chlorinated gutta percha and gum chicle, thus:

ml. benzene	ml. dibutyl phthalate	gms. chlorinated pale crepe	Notation
100	10	20	E 2 P.
100	16	20	E 3 P.
100	16	20	E 4 P.

In addition to the above samples, there were obtained from the Hercules Powder Co. Inc., U.S.A., three types of commercial chlorinated pale crepe (Tornesit). Solutions of these were used for impregnation, for the purpose of comparing the commercial product with our laboratory prepared samples. Solution concentrations, and notation, follow:-

ml. benzene	ml. dibutyl phthalate	gms. Tornesit	viscosity TYPE. (Centipoises)	notation.
100	14	20	6	6 T
100	14	20	8	8 T
100	14	20	20	20 T

(b) Method of Impregnation:- 6-foot lengths of strand were cut, coiled very loosely into coils of 2 inches in diameter, and stacked loosely in 200 ml. beakers. The impregnating solutions were poured into the labelled beakers, and strands soaked for 10 minutes. They were then hung up to dry for 1 week, after which they were immersed in the sea. (Peters (29) states that 1 week must elapse before testing chlorinated rubber films.)

(c) Method of Immersion in Sea:- A board, 6 feet by 1 foot by 2 inches, through which were bored 60 one-half inch holes, was floated at the Vancouver Yacht Club, Coal Harbour. The treated strands (6-foot lengths) were suspended, through these holes, in the sea-water. One inch diameter, numbered, brass tags, coated with chlorinated rubber, were tied to one end of strands, and No. 7 ringed sinkers to the other end. The sinkers effectively prevented tangling of the immersed strands (a sinker and label was not attached to each strand. Ten measurements of tensile strength were required for each kind of treatment. One measurement required 3 feet of strand, hence, 5 strands (6 feet each) were tied together).

Results of Immersion Tests on
Strands Coated with the Various Chlorinated Rubbers.

(All measurements of tensile strength
are in lbs., and are on dry strand.)

TABLE I

(Strands were immersed January-February, 1939).

Tensile Strength (lbs.)								
Notation	Before Immersion in sea		Immersed Two Weeks in sea		Immersed Four Weeks in sea		Immersed Nine Weeks in sea	
A 1	31.45	2.24	21.3	1.53	6.9		0	
A 2	34.90	3.07	26.2	3.88	< 5		0	
A 3	36.34	2.87	26.1	4.63	< 5		0	
A 5	36.85	3.26	24.1	3.30			0	
A 6	34.75	5.06	18.2	3.05	< 5		0	
B 1			22.4	3.90	< 5		0	
B 2	35.55	3.06	19.6	2.47	< 5		0	
D 1	35.90	4.09	9.3	0.46	< 5		0	
D 2	34.60	3.85	22.4	3.43	< 5		0	
E 2	37.50	3.46	24.9	3.33	< 5		0	
E 4	38.56	2.48	23.2	4.30	< 5		0	
E 2 P	37.25	2.69	28.6	4.38	19.8	5.68	< 5	
E 3 P	34.00	3.09	28.9	4.10	18.9	2.83	< 5	
E 4 P	33.65	3.65	24.8	3.92	12.7	2.26	< 5	
6 T	35.80	4.60	30.4	2.62	16.5	3.54	< 5	
8 T	34.35	1.48	29.8	2.58	10.8	4.92	< 5	
20 T	32.40	3.51	28.9	2.73	21.9	2.11	< 5	
Control	33.65	2.10	12.5	2.94	0		0	

From the experimental results given in Table I, it is possible to draw the following two conclusions:

1. Tornesit, the commercially produced chlorinated rubber, is more effective as a preservative than any chlorinated product, made in this laboratory, from gum chicle or gutta percha. The chlorinated product, made in this laboratory, from pale crepe has the same effectiveness as Tornesit as a preservative. This is to be expected, since both constitute essentially the same compound. Both, moreover, are of essentially the same degree of purity. It seems most probable that the ineffectiveness of the chlorinated products made from gum chicle and gutta percha is due to the impurities in the gum chicle and gutta percha.

2. Comparing sample E 2 with E 2 P, and comparing E 4 with E 4 P, it is seen that the preservative coatings on E 2 P and E 4 P were much superior to those on E 2 and E 4, respectively. Below are restated for convenience the compositions of the solutions used to impregnate these four samples:-

	ml. of benzene	gms. of chlorina- ted rubber	c.c. of dibutyl phthalate	tensile strength of impregnated strand after four weeks immersion in sea water.
E 2	100	20	6	< 5 lbs.
E 2 P	100	20	10	19.8 lbs.
E 4	100	20	6	< 5 lbs.
E 4 P	100	20	16	12.7 lbs.

It is at once apparent that the concentration of plasticiser (dibutyl phthalate) is a highly important factor in the preservative qualities of a film of chlorinated rubber.

Extent of knot slippage:- Before continuing with the investigation, it was highly important to be certain the treatment of nets, with chlorinated rubber, produced no tendency for the knots of the net to slip. A number of solutions were prepared, in which concentration of chlorinated rubber, concentration of plasticiser, type of chlorinated rubber were, in turn, varied. Results, together with the respective solutions used, are recorded in Table II. 5/40 linen gill netting was used, and each treatment received eight tests for slippage. Only when all eight tests failed to reveal slippage was the slippage recorded as "none" in the Table.

Nets were immersed for ten minutes in the solutions, dried one week, and tests made on wet net (soaked fifteen hours in tap water).

TABLE II

Conc. of Plasticiser in c.c.s. per 100 grams of benzene	Type of Chlorinated rubber (Tornesit) (Centipoises)	Conc. of Chlorinated rubber in grams per 100 grams of benzene	Extent of Knot Slippage
9.0	7	15	none
12.0	7	20	"
15.0	7	25	"
18.0	7	30	"
8.5	13	14	"
11.5	13	19	"
14.6	13	24	"
17.0	13	28	"
5.5	157	9	"
7.9	157	13	"
10.9	157	18	"
14.0	157	23	"
3.4	1225	6	appreciable
5.0	1225	9	very slight
7.3	1225	13	none
9.0	1225	16	"
16.3	7	25	trace
15.0	7	25	none
13.8	7	25	"
12.5	7	25	"
15.8	13	24	appreciable
14.6	13	24	none
13.3	13	24	"
12.1	13	24	"
11.4	157	18	"
10.9	157	18	"

(cont'd)

TABLE II (cont'd)

Conc. of Plasticiser in c.c.s. per 100 grams of benzene	Type of Chlorinated rubber (Tornesit) (Centipoises)	Conc. of Chlorinated rubber in grams per 100 grams of benzene	Extent of Knot Slippage
9.5	157	18	slight
8.5	157	18	"
8.3	1225	13	very slight
7.3	1225	13	none
6.8	1225	13	trace
6.3	1225	13	none

trace = less than 0.2 cm. slip.
 very slight = less than 0.5 cm. slip.
 slight = slips 0.5 cm.
 appreciable = greater than 1 cm. slip.

Results show that there is no slippage of knots with those solutions which would be of use as a preservative. Slippage only occurs when the concentration of plasticiser is so great that the nets would in any case be useless due to extreme stickiness.

The Effect of the Plasticiser on the Preservative Properties of the Chlorinated Rubber Film.

Since, as was shown above, the concentration of plasticiser effects the preservative qualities of the chlorinated rubber film, a short study was next undertaken in an attempt to determine first, if the kind of plasticiser was significant, and second, which concentration of plasticiser was most suitable.

There have been recommended a very large number of plasticisers for chlorinated rubber. Twiss and Wilson (30) suggest metallic halides, oils, turpentine, chloronaphthalenes, tritolyl phosphate, organic esters, ethereal oils, cellulose plastic softeners, synthetic resins or varnishes. For textile fabrics, Teague (31) uses coumarone resin and tritolyl phosphate. Ellis (32) lists the following types of plasticisers: drying oils (e.g., linseed, tung, soya bean), non-drying oils (e.g., palm, raw castor), fatty acid esters (e.g., butyl and amyl stearates), hydrogenated or unhydrogenated alkyl or aralkyl esters of abietic acid (e.g., Hercolyn), adipic acid esters (e.g., Sipalins), phthalic acid esters (e.g., dibutyl phthalate), phosphoric acid esters (e.g., triphenyl and tricresyl phosphates), citric acid esters (e.g., triethyl citrate), chlorinated aromatics (e.g., Aroclors).

From this large list of plasticisers, the following were chosen for investigation: dibutyl phthalate, iso amyl stearate, and tricresyl phosphate.

Following are the solutions used for impregnating, and the procedure used in impregnating the strands of fishing twine:

A 25 per cent. by weight solution of chlorinated rubber (17 c.p.s. Tornesit) in benzene was prepared. By per cent. by weight we shall always in this paper mean

grams of solvent (benzene). Twenty-five per cent. by weight thus represents 25 grams of Tornesit to 100 grams of benzene. To this solution was added the appropriate amount of plasticiser, as shown in column (3) Table III below. The resulting solution was mixed thoroughly. Strands of 5/40 linen twine were immersed in the various solution for 10 minutes, then dried for one week. The strands were then immersed in the sea, in accordance with the method described on page (20).

Table III, columns 4, 5 and 6 record the breaking strength of the strands impregnated with solutions described in Table III, column 3. In this series all strands were broken wet. The strands broken without immersion in sea-water were broken wet after immersion for fifteen hours in tap water. Those strands immersed in the sea were broken wet immediately after being taken from sea (they were washed in tap water).

TABLE III

Notation For Samples	Plasticiser Used	Volume of Plasticiser in c.c., per 100 cc of 25% Chlorinated Rubber Solution	Not Immersed in Sea	Tensile Strength (lbs).	
				Immersed in Sea, 4 weeks March, 1939	Immersed in Sea 9 weeks (March- April)
1	dibutyl phthalate	8	64.0	34.9	4.4
2	do do	11	57.7	55.7	35.0
3	do do	14	53.5	44.7	7.6
4	iso amyl stearate	6	60.9	15.3	0
5	do do	12	56.2	45.7	5
6	do do	14	51.9	47.9	0
7	do do	16	41.3	25.7	0
8	tricresyl phosphate	14	53.0	42.4	3
9	do do	17	57.1	32.6	2
10	do do	20	45.1	20.8	0

From the results listed in Table III, the following important conclusions can be drawn:

1. The kind of plasticiser has an important bearing on the preservative qualities of the chlorinated rubber film. Dibutyl phthalate is much superior to iso amyl stearate or tri cresyl phosphate.

2. In the cases of dibutyl phthalate and iso amyl stearate there is an optimum concentration of plasticiser at which the film has its greatest preservative power. A change as slight as 2 per cent. in the concentration on either side of this optimum concentration markedly lowers the preservative qualities of the film. (Had a suitable range of concentration been used for tri cresyl phosphate, it presumably would also exhibit an optimum concentration). The data in Table III is too meagre to permit plotting of graphs to find by interpolation the exact optimum concentrations for the two plasticisers. The experimental work recorded is, then, to be considered as preliminary. More extensive data will have to be obtained on the subject.

3. In the case of dibutyl phthalate and iso amyl stearate, the tensile strength of the wet strand, before immersion in the sea, decreased as the per cent. plasticiser in the chlorinated rubber film increased. Since a wet, untreated strand has a much greater tensile strength than a dry, untreated strand, it is most probable that the greater the concentration of plasticiser used, the more impermeable to water is the chlorinated rubber film. The tensile strength of a treated strand would, therefore, be a function of the time of immersion in water.

Further Investigation of Plasticisers.

Time would not permit a thorough investigation of plasticisers this year. It seemed desirable, however, to at least establish, approximately, the optimum concentration of one plasticiser, in order that this optimum concentration may be used in other phases of the research. Three types of Tornosit were used, 7, 13 and 157 centipoises. Since the linear density of the treated strand increases as the viscosity of the Tornosit solution increases, the concentrations of the solutions of the three types of Tornosit were not made the same, but were so chosen that

the linear density of the treated strands were as nearly the same as possible after treatment with solutions made from the three different types of Tornosit. In this way a suitable basis was established whereby the three types of Tornosit could be compared one with the other, with respect to preservative power.

Procedure:- Tornosit was dissolved in benzene, dibutyl phthalate added in varying concentrations, strands immersed ten minutes, then dried one week.

Number of Sample	Viscosity Type of Tornesit	Grams of Tornesit in 100 grams of benzene	C.C. Dibutyl Phthalate in 100 grams of benzene	Linear Density of strand in grams per metre (approx)	TENSILE STRENGTH (LBS.) Broken Wet		
					Before Immersion in sea	Immersed in sea 3 weeks (April)	Immersed in sea 7 weeks (April, May)
1	7	20	8	0.66		30.8	5.0
2	7	20	11	"		39.3	18.4
3	7	20	13	"		38.8	18.0
4	7	20	14	"		37.2	18.1
5	7	20	16	"		28.0	15.7
6	13	19.8	8	0.65		35.5	5.0
7	13	19.8	11	"		46.3	28.4
8	13	19.8	12.9	"		44.2	26.2
9	13	19.8	14	"		35.5	23.1
10	13	19.8	16	"		33.1	20.6
11	157	19.0	7.5	0.67		47.9	13.1
12	157	19.0	10.5	"		47.7	44.8
13	157	19.0	12.3	"		48.6	35.8
14	157	19.0	13.5	"		49.7	35.3
15	157	19.0	15.0			33.8	27.2

TABLE IV

Graphs A shows the loci of data in Table IV. Per cent. plasticiser being plotted against tensile strength of strand. The conclusions to be reached from these loci are:

By "optimum" concentration of plasticiser we shall mean the concentration which, when used in the Tornesit film, gives to a strand the maximum tensile strength after a period of immersion in the sea. In tabular form are presented the optimum concentrations of plasticiser, as found, by interpolation, from Graphs A:

Type of Tornesit	Optimum Concentration of dibutyl phthalate in c.c. per 100 gms. benzene	Optimum Ratio of c.c. dibutyl phthalate to gms. of Tornesit.
7	11.5	0.575
13	11.1	0.561
157	10.7	0.563

The optimum concentration of plasticiser is seen from the graphs to be independent of the time of immersion of the strands in the sea. Thus the locus of tensile strength against per cent. plasticiser gives the same maximum tensile strength with respect to per cent. plasticiser, for three weeks as for seven weeks immersion.

The appearance of maxima in every locus confirms the indication on page (28), that such maxima exist. The cause of maxima has not been investigated in this research.

Thirteen cps. Tornesit is seen to be definitely superior to 7 cps. Tornesit. While 157 cps. Tornesit appears most superior, the data is much more inaccurate than for the other two types, and it is inadvisable to draw very certain conclusions from such data. Due to the higher viscosity of the 157 cps. Tornesit solution,

strands were more unevenly coated, apparently, than with lower viscosity solutions. In any case, 157 cps. Tornesit solutions are, in the concentrations needed, far too viscous to be of practical value, for the handling of a net during the process of impregnation, and would be very difficult with solutions of such high viscosity. (It was for this reason 1,000 cps. Tornesit was not experimented with).

Effect of Time of Immersion of Strand in
Impregnating Solution on the Life of the Strand in the Sea

5/40 linen gill net twine was soaked for various periods of time in solutions consisting of a mixture of Tornesit and dibutyl phthalate (plasticiser) in benzene (solvent). The treated strands were dried in air one week before immersion in the sea.

Three viscosity types of Tornesit were tested. Since thickness of the film on the treated strand increases with viscosity of impregnating solution, the concentration of each of the three types of Tornesit was so chosen that the linear densities of the strands, treated with the three types of Tornesit, were approximately equal. This enabled a comparison to be made of the relative effectiveness of the different types of Tornesit.

In Table V, columns (3) and (4) give the composition of the impregnating solutions. The ratio of Tornesit to plasticiser was constant for all three viscosity types.

In columns 7 and 8 of Table V are given the tensile strengths of the treated strands after three weeks, and seven weeks, respectively, immersion in the sea. Each figure given for tensile strength represents the average for ten samples of strand. In column (7) are given, in addition to the tensile strengths, the corresponding "standard deviations". Examination of these reveals the wide fluctuations in sampling. Applying the criterion described on page (11), we are able to decide from the data in Table V whether time of immersion in impregnating solution affects the life of the treated strand in the sea. We arrive at the following conclusions:

(1) Using 7 cps. or 13 cps. types Tornesit, time of immersion of strand in impregnating solution has little, if any, effect on the preservative qualities of the Tornesit coating, within the time limits of 2 minutes to 6 hours. This can probably be correctly interpreted as meaning that the impregnating solution, while it coats probably the finest of the fibres of linen, never-

TABLE V.

Tensile Strength of
Strands in Lbs.
Broken Wet

Notation of Sample	Viscosity Type of Tornesit (Centipoises).	Grams of Tornesit per 100 Grams of Benzene	m.l. of Dibutyl Phthalate Per 100 Grams of Benzene	Time of Immersion of Strand in Tornesit Solution	Linear Density of Treated Strands Grams per Metre	Immersed in Sea 3 Weeks April, 1939	Immersed in Sea 7 Weeks April - May, 1939.
						Standard Deviation	Standard Deviation
1	7	20	13	2 min.		40.6	4.45
2	7	20	13	10 "		40.0	6.41
3	7	20	13	30 "		38.3	4.74
4	7	20	13	2 hours		38.1	4.23
5	7	20	13	6 "	34	37.6	5.21
6	13	19.8	12.9	2 min.		45.8	4.86
7	13	19.8	12.9	10 "		44.0	5.86
8	13	19.8	12.9	30 "		43.4	3.86
9	13	19.8	12.9	2 hours		41.6	6.03
10	13	19.8	12.9	6 "		45.4	4.23
11	157	19.0	12.3	2 min.		43.8	7.21
12	157	19.0	12.3	10 "		43.8	6.03
13	157	19.0	12.3	30 "		50.2	4.22
14	157	19.0	12.3	2 hours		49.4	6.30
15	157	19.0	12.3	6 "		55.9	4.59

theless does not diffuse through the walls of the individual fibres.

(2) Using 157 cps. type Tornosit, time of immersion in impregnating solution is a factor in the life in the sea of the treated strand. The life of the strand in the sea increases with increasing time of immersion in impregnating solution in this case. Apparently the strand should be left in impregnating solution at least 30 minutes and preferably at least 6 hours. This conclusion, of course, can be considered true only for the concentration of Tornosit solution used (19 grams of 157 cps. Tornosit in 100 grams Benzene), but it doubtless holds for somewhat lower concentrations, and certainly for higher. The conclusion that life of the strand in the sea increases with increasing time of immersion is, in fact, to be expected, since the impregnating solution in this case was quite viscous, and penetration of it through the fine mesh of fibres of the strand would be slow.

Effect of Concentration of Tornosit

Solution on the Life of the Strand in the Sea.

Impregnating solutions consisted of mixtures of Tornosit, dibutyl phthalate (plasticiser) and benzene (solvent). Three viscosity types of Tornosit were examined. For every impregnating solution given in Table VI, the ratio of Tornosit (in grams) to dibutyl phthalate (in m.l.) was constant.

From Table VI can be drawn the following conclusions:

(1) For 7 cps. Tornosit the life of the strand in the sea increases markedly as the concentration of Tornosit in benzene increases, up to a concentration of 25 grams of Tornosit in 100 grams of benzene. At least this concentration of Tornosit solution is, therefore, to be recommended.

(2) For 13 cps. Tornosit a concentration of at least 20 grams of Tornosit in 100 grams of benzene is

TABLE VI.

Notation of Sample	Viscosity Type of Hornesit (cp.).	Grams of Hornesit in 100 grams of Benzene	ml. of Di- butyl Phth- alate in 100 grams of Benzene	Linear Density of Treated Strand (grams per metre).	Tensile Strength of Treated Strands (lbs.) Broken Knot			
					Immersed in Sea 3 Weeks April, 1939	Immersed in Sea 7 Weeks April May, 1939	Immersed in Sea 7 Weeks April May, 1939	Immersed in Sea 7 Weeks April May, 1939
						Standard Deviation		Standard Deviation
1	7	10	6.5	0.55	29.1	3.40	0.1	----
2	7	15	9.8	0.59	32.1	3.34	18.1	4.83
3	7	20	13.0	0.66	37.9	4.24	24.0	4.00
4	7	25	16.3	0.74	39.9	5.19	31.0	6.03
5	7	30	19.5	0.84	46.5	6.53	32.0	5.14
6	13	8	5.2	0.46	27.4	3.08	0.0	----
7	13	14	9.2	0.59	35.1	3.86	25.5	6.09
8	13	19	12.4	0.62	44.1	4.37	32.5	4.84
9	13	24	15.7	0.67	46.1	3.81	40.2	5.21
10	13	28	18.3	0.80	45.4	4.35	39.2	4.23
Untreated Strand	--	--	----	0.44	0.0	----	----	----

to be recommended, for the same reason as that given in the above paragraph.

(3) In deciding which of the two types of Tornosit is superior as a preservative, it is necessary to compare the tensile strengths (given in columns (6) and (7) Table II) of treated strands possessing the same linear densities after treatment with the two types of Tornosit. Graphs I show linear density (from column (5), Table VI) plotted against tensile strengths (from columns (6) and (7), Table II). From these graphs it is clear that both for the data obtained when the strands were immersed for three weeks, and that for seven weeks immersion, the 13 cps. type Tornosit is superior as a preservative to the 7 cps. type Tornosit. (It is well to point out, however, that the mean deviations listed in columns (6) and (7) of Table II are large, and consequently Graphs I are of little value except to obtain qualitative statements).

(4) The strands whose tensile strengths are listed in column (7), Table VI, were "broken" five months after taking from the sea. On taking from the sea they were washed well in tap water, dried, and stored dry. Comparing the tensile strengths of sample No. 3, Table VI, and sample No. 3 Table V, we see that storing the treated strands dry for five months has no apparent effect on their tensile strengths. Again, comparing the tensile strengths, after seven weeks immersion in the sea, of sample No. 8 Table VI and sample No. 7, Table V, we find no significant difference in tensile strengths of the two samples. Hence again we reach the conclusion that storing the treated strand has no apparent effect on its tensile strengths.

Effect of Impregnating Strands with Toxic Salts Before Coating with Chlorinated Rubber.

Since it is most probable that bacterial action usually makes the most important contribution to net-rotting, it seemed natural that impregnation of the strands with a salt toxic to bacteria, followed by a coating of chlorinated rubber, should prove more effective in retarding rotting than a coating of chlorinated rubber alone. Moreover, the chlorinated rubber coating should retard the rate of washing out of the toxic salt.

It was decided to treat the strands with salts of silver, mercury, and copper. The salts of these metals were chosen arbitrarily. In addition some strands were impregnated with colloidal silver, since this has been shown to be toxic to bacteria. Thus Filippi (33) has reported the following as the lethal concentrations of colloidal metals, on certain protozoa:--

Sol.	Lethal Concentration of Metal For	
	Paramecium	Vorticella
Silver	1 : 450,000	1 : 170,000
Mercury	1 : 390,000	1 : 92,000
Copper	1 : 70,000	1 : 36,000
Nickel	1 : 24,000	1 : 9,500
Gold	1 : 4,000	1 : 4,000

That the therapeutic action of silver sols is generally due to the metallic ions in solution, was pointed out by Ascoli and Izar (34), Paul (35) and Sollman and Pilcher (36). It seems uncertain yet whether the metal itself has any therapeutic effect independent of its property of producing ions.

Following are the procedures followed in treating the strands. When the treatment includes the words "coated with Tornosit", this means the strands were treated with toxic salt, dried and then impregnated with a Tornosit solution for 10 minutes. The Tornosit solution had the following composition:--

Tornosit (16 cps.)	20 grams.
benzene	100 grams.
dibutyl phthalate	11.4 c.c.

After impregnation with this solution the strands were dried for 1 week prior to immersion in the sea.

TABLE VII

Notation	Treatment
1.	Soaked for 30 minutes in 0.001 N silver nitrate. Dried 1 week. Coated with Tornosit.
2.	Soaked for 30 minutes in 0.01 N silver nitrate. Dried 1 week. Coated with Tornosit.
3.	Soaked for 30 minutes in 0.001 N silver nitrate, then for 30 minutes in 0.0002 N sodium chloride. Washed by immersing for 3 twelve-hour periods in tap water. Dried 1 week. Coated with Tornosit.
4.	Soaked for 30 minutes in 0.001 N silver nitrate, then for 30 minutes in 0.002 N sodium chloride. Washed by immersing for 3 twelve-hour periods in tap water. Dried 1 week. Coated with Tornosit.
5.	Soaked for 30 minutes in 0.01 N silver nitrate, then for 30 minutes in 0.02 N

Notation	<u>TABLE VII</u> (cont'd) Treatment
	sodium chloride. Washed by immersing for 3 twelve-hour periods in tap water. Dried 1 week. Coated with Tornosit.
6.	A solution of silver ammonium chloride was prepared by adding to a 0.01 N silver nitrate solution, an equivalent amount of ammonium chloride, then dissolving the precipitated silver chloride by adding an excess of ammonium hydroxide (1 : 1). Strands were soaked for 30 minutes in the resulting solution, then dried 1 week. Coated with Tornosit.
7.	Soaked for 30 minutes in 1.0 N copper sulphate; dried 1 week. Coated with Tornosit.
8.	Soaked for 30 minutes in 0.1 N copper sulphate; dried 1 week. Coated with Tornosit.
9.	Soaked for 30 minutes in 0.01 N copper sulphate; dried 1 week; coated with Tornosit.
10.	Soaked for 30 minutes in 0.001 N mercuric chloride; dried 1 week; coated with Tornosit.
11.	Soaked for 30 minutes in 0.01 N mercuric chloride; dried 1 week. Coated with Tornosit.
12.	Soaked for 30 minutes in 0.1 N mercuric chloride; dried 1 week; coated with Tornosit.
13.	Soaked for 30 minutes in 0.1 N mercuric chloride, to 200 ml. of which solution

TABLE VII (cont'd)

Notation	Treatment
	had been added 12 ml. of 10 per cent. gum arabic; then dried 1 week; coated with Tornesit.
14.	Soaked for 30 minutes in 0.1 N mercurous nitrate, then for 30 minutes in 3 N sodium chloride, then washed by immersing strands for 3 twelve-hour periods in tap water. Dried; coated with Tornesit.
15.	Soaked for 30 minutes in 0.0001 N silver nitrate, then for 15 minutes in saturated hydrogen sulphide water, then washed strands by immersing in tap water for 5 twelve-hour periods. Dried; coated with Tornesit.
16.	Same treatment as No. 15, except that 0.001 N silver nitrate was used.
17.	Same treatment as No. 15, except that 0.01 N silver nitrate was used.
18.	Same treatment as No. 15, except that 0.1 N silver nitrate was used.
19.	Soaked in 0.0001 N silver nitrate, then in 1 per cent. tannin (aqueous solution), then washed by immersion for 3 twelve-hour periods in tap water. <u>No Tornesit coating applied.</u>
20.	Same as No. 19, except that 0.01 N silver nitrate was used. <u>No Tornesit coating applied.</u>
21.	Same as No. 19, except that <u>Tornesit coating was applied.</u>

TABLE VII (cont'd)

Notation	Treatment
22.	Same as No. 20, except that <u>Tornesit coating was applied.</u>
23.	Soaked for 1 hour in a solution consisting of 30 grams of copper naphthenate (Standard Oil Co. sample) per 100 ml. of thinner S.O. 350 (Standard Oil Co. sample). <u>No Tornesit coating applied.</u>
24.	Same as No. 23, except that 10 grams of copper naphthenate per 100 ml. of thinner S.O. 350 was used. <u>No Tornesit coating applied.</u>
25.	Same as No. 23, except that 1 gram of copper naphthenate per 100 ml. of thinner S.O. 350 was used. <u>No Tornesit coating applied.</u>
26.	Same as No. 24, except that <u>Tornesit coating was applied.</u>
27.	Soaked for 10 minutes in the Tornesit solution (composition on page 39), to each 100 ml. of which had been dissolved 1 gram of copper naphthenate.
28.	Soaked for 10 minutes in the Tornesit solution (composition on page 39) to each 100 ml. of which had been dissolved 10 grams of copper naphthenate.
29.	Soaked for 10 minutes in the Tornesit solution (composition on page 39), to each 100 ml. of which had been dissolved 0.01 gram of silver naphthenate (see below for preparation).

TABLE VII (cont'd)

Notation	Treatment
30.	Soaked for 10 minutes in the Tornesit solution (composition on page 39) to each 100 ml. of which had been dissolved 0.1 gram of silver naphthenate.
31.	Soaked for 10 minutes in the Tornesit solution (composition on page 39) to each 100 ml. of which had been added 1 gram of silver naphthenate.
32.	Soaked for 30 minutes in 0.1 N mercurous nitrate, then for 30 minutes in saturated hydrogen sulphide water, then washed for 4 twelve-hour periods in tap water. Dried; coated with Tornesit.
33.	Coated with Tornesit, only.
34.	Strand untreated in any way.
35.	

Preparation of Silver Naphthenate.

Thirty grams of naphthenic acid (Standard Oil Co. sample - "50 naphtone acid A") were measured out. A solution of potassium hydroxide (7.77 grams of KOH dissolved in 500 ml. water) were stirred into the acid. The resulting mixture was thoroughly stirred. A solution of silver nitrate (23 grams of silver nitrate in 200 ml. water) was slowly stirred into the potassium naphthenate solution. Silver naphthenate precipitated in white flocks. Stirred for one-half hour. Filtered at pump. Washed silver naphthenate thoroughly. Dried. Preserved the resulting white powder in the dark. (silver naphthenate is not made commercially).

INAPHTHENATE

Results of sea-immersion tests on strands treated as described in Table 7, are given in Table 8. The numbers of the samples in Table 8 correspond to the same numbers in Table 7. For convenience, however, an abbreviated description of treatments is given in Table 8, Column 1.

TABLE 8.

(All strands coated with Tornesit except where otherwise noted)

TOXIC SALT USED (see Table 7)	Notation (see Table 7)	TENSILE STRENGTH (LBS.) Broken Wet.					
		Before Immer- sion in sea.		Immersed in Sea 5 Weeks Jan - Feb. 1940		Immersed in Sea 10 WEEKS	
				Standard Deviation	Standard Deviation	Standard Deviation	Standard Deviation
0.001 N AgNO ₃	1	57.8	2.79	33.6	6.63	21.2	5.69
0.01 N AgNO ₃	2	55.8	5.16	42.7	6.86	35.3	6.08
AgCl	3	56.3	4.44	45.4	2.76	27.3	8.13
AgCl	4	54.7	3.02	39.7	6.25	10.9	4.02
AgCl	5	58.0	4.90	51.4	5.61	40.3	14.01
Ag(NH ₃) ₂ Cl	6	54.2	4.17			28.2	6.97
1.0 N CuSO ₄	7	54.1	2.59	51.5	3.87	21.6	5.26
0.1 N CuSO ₄	8	56.3	5.73	40.8	5.51	21.9	6.85
0.01 N CuSO ₄	9	51.2	3.50	34.3	2.92	12.3	4.76
0.001 N HgCl ₂	10	54.9	2.95	42.6	4.40	23.7	5.90
0.01 N HgCl ₂	11	54.6	3.84	47.7	5.77	37.2	7.41
0.1 N HgCl ₂	12	51.3	4.77	50.9	6.12	27.6	5.69
HgCl ₂ Gum Arabic	13	55.2	3.65	34.8	2.72	12.0	4.14
HgCl	14	52.4	3.41	40.8	2.30	20.1	5.23

(cont'd)

TABLE 8 (con'td)

(All strands coated with Tornesit except where otherwise noted)

TOXIC SALT USED (see Table 7)	Notation (see Table 7)	TENSILE STRENGTH (LBS.) Broken Wet.					
		Before Immer- sion in sea.		Immersed in Sea 5 Weeks Jan - Feb 1940		Immersed in Sea 10 WEEKS.	
				Standard Deviation	Standard Deviation	Standard Deviation	Standard Deviation
0.0001 N AgNO ₃ - H ₂ S	15	57.8	4.86	41.4	4.73	18.8	6.40
0.001 N AgNO ₃ H ₂ S	16	58.6	5.66	50.0	3.96	29.9	7.03
0.01 N AgNO ₃ H ₂ S	17	52.8	4.22	41.0	6.80	21.6	9.72
0.1 N AgNO ₃ - H ₂ S	18	51.2	3.46	44.8	4.16	31.3	7.10
0.0001 N AgNO ₃ - Tannin							
No Tornesit	19	52.0	5.46	0.0	--	0.0	--
0.01 N AgNO ₃ - Tannin							
No Tornesit	20	54.3	3.26	0.0	--	0.0	--
0.0001 N AgNO ₃ - Tannin	21	58.6	4.29	48.0	4.55	36.3	7.72
0.01 N AgNO ₃ - Tannin	22	51.4	4.34	56.7	3.46	49.2	7.41
30% Cu Naphthenate							
No Tornesit	23	55.0	2.90	24.0	5.16	0.0	--
10% Cu Naphthenate							
No Tornesit	24	51.7	2.57	5.0	--	0.0	--
1% Cu Naphthenate							
No Tornesit	25	54.1	4.06	5.0	--	0.0	--
10% Cu Naphthenate	26	54.8	5.89	57.6	5.26	45.5	7.52
1% Cu Naphthenate							
In Tornesit soln.	27	56.3	6.35	56.1	4.26	54.8	3.90
10% Cu Naphthenate							
In Tornesit soln.	28	57.0	5.05	53.4	5.33	38.4	10.3

46.

(cont'd)

TABLE 8 (cont'd)

(All strands coated with Tornesit except where otherwise noted)

TOXIC SALT USED (see Table 7)	Notation (see Table 7)	TENSILE STRENGTH (LBS.) Broken Wet					
		Before Immer- sion in sea.		Immersed in Sea 5 Weeks Jan - Feb 1940		Immersed in Sea <i>10</i> WEEKS.	
				Standard Deviation		Standard Deviation	
0.01% Ag Naphthenate In Tornesit soln.	29	56.3	4.73	48.0	6.33	29.6	8.00
0.1% Ag Naphthenate In Tornesit soln.	30	55.5	4.25	53.4	6.54	33.8	7.17
1% Ag Naphthenate In Tornesit soln.	31	55.2	5.03	57.0	6.26	50.1	4.82
HgNO ₃ - H ₂ S	32	53.1	3.24	51.6	5.90	26.2	11.6
No Toxic Salt	33	58.8	2.20	48.4	6.45	29.2	6.85
Control	34	51.9	--	0.0	--	0.0	--

Before discussing the most important conclusion to be reached from Table 8, namely, the choice of most effective preservative, two conclusions of minor importance, but still of interest, may be noted.

(1) Comparison of Nos. 12 and 13 shows that gum arabic is detrimental when in contact with the strands. The original reason for the addition of gum arabic was that it might act as a protective colloid for the mercuric chloride, thus giving a finer dispersion of particles, and hence a more uniform impregnation with toxic salt, than would be possible without it. That its presence is detrimental, may perhaps be attributable to its being a polysaccharide, and in consequence a medium for bacterial growth.

(2) Comparison of Nos. 9, 10 and 11, with No. 33, shows that copper sulphate when in permanent contact with the strands has no resultant preservative value, but, probably in high concentrations, and certainly in concentrations as low as 0.01 N, is detrimental. The cause of the weakening effect of this salt on the strength of the strands is doubtless the sulphuric acid formed on hydrolysis.

The most important conclusion to be reached from data in Table 8 is that several preservatives listed there are better than the commonly used commercial preservative copper naphthenate. Samples No. 23, 24, and 25 in Table 8 refer to strands treated with copper naphthenate in concentrations 30%, 10% and 1%, respectively. In no case was the treatment as effective as treatment with chlorinated rubber (sample No. 33, Table 8). It is, therefore, to be concluded that, with respect to simple sea-immersion tests at least, a chlorinated rubber treatment preserves strands much longer than a copper naphthenate treatment. In most cases preliminary treatment of the strand with a toxic salt, followed by treatment with chlorinated rubber, did not prove any more effective than the treatment of the strand with chlorinated rubber alone (In deciding if addition of a toxic salt is beneficial, the standard

TENSILE STRENGTH OF STRAND, IN LBS., BROKEN VVET.

60

50

40

30

20

10

0

0

2

4

6

8

10

NO. OF WEEKS STRANDS WERE
IMMERSED IN SEA.

1% COPPER NAPHTHENATE
IN 20% SOLN. OF
13 C.P.S. TORNESIT.

20% SOLUTION OF
13 C.P.S. TORNESIT.

30% COPPER
NAPHTHENATE SOLN.

UNTREATED
STRAND.

deviations, together with the "criterion" described on page 11, should be used. Notable exceptions to the ineffectiveness of toxic salts are treatments Nos. 22, 26, 27, 28 and 31. The tensile strengths of each is, after ten weeks immersion in the sea, greater than that of No. 33 (chlorinated rubber only). No. 28 has a standard deviation so large, however, that comparison of it with these other treatments is unfortunately valueless. There is no difficulty, fortunately, in deciding which of Nos. 22, 26, 27 and 31, is the best treatment to use. Consideration of cost at once enables us to select No. 27 as the most satisfactory treatment.

The graph opposite illustrates the superiority of treatment No. 27 over the commonly used commercial preservative Copper Naphthenate alone.

Further Investigation on Plasticisers.

On pages 27 and 30 of this report there appear results obtained on using as plasticisers, for Tornosit, dibutyl phthalate, isoamyl stearate, and tricresyl phosphate. Since it was proved there that the life of a strand in the sea was not only a function of the concentration of plasticiser used, but also of the kind of plasticiser, it was decided to now test several commercially available plasticisers.

TABLE 9.

Conc. of Tornosit: 20 grams of Tornosit per 100 Grams of Benzene

 τ_1 = Difference between tensile strength before, and after 4 weeks, immersion. τ_2 = Difference between tensile strength before, and after 7 weeks, immersion.

Notation	Plasticiser	ml. of Plasticiser per 100 ml. Tornosit Solution	TENSILE STRENGTH (LBS.): BROKEN WET						
			Before Immersion in Sea		Immersed in Sea 4 weeks (March, 1940)		Immersed in Sea 7 Weeks (March-April, 1940)		
				Standard Deviation		Standard Deviation	τ_1		Standard Deviation τ_2
1	Santiciser M 17	9			24.9			0.0	6.08
2	" M 17	11			40.8			15.0	
3	" M 17	13			28.4			5.0	
4	Dow No. 5	9			19.3			0.0	
5	" No. 5	11			31.5			5.0	
6	" No. 5	13			30.1			5.0	
7	" No. 5	15			37.1			17.3	4.47
8	" No. 5	17			39.7			17.2	2.44
9	" No. 5	19			27.7			5	
10	Tri Cresyl Phosphate	4			8.0			5	
11	" " "	8			17.0			5	
12	" " "	10			24.1			5	
13	" " "	12			37.6			5	
14	" " "	14			19.8			5	
15	" " "	16			10.7			0.0	
16	n-Butyl Stearate	4			8.7			0.0	
17	" "	6			16.3			0.0	
18	" "	8			16.6			0.0	
19	" "	9			19.0			0.0	
20	" "	10			14.0			0.0	
21	" "	11			22.0			0.0	

(cont'd)

TABLE 9. (cont'd)

Notation	Plasticiser	ml. of Plasti- ciser per 100 ml. Tornesit Solution	Before Immersion In Sea		Immersed in Sea 4 weeks (March 1940)			Immersed in Sea 7 Weeks (March-April, 1940)		
				Standard Deviation		Standard Deviation	$\bar{T}$		Standard Deviation	$\bar{T}_2$
22	Aroclor No. 1242	6	59.1	3.54	28.9	3.72	30.2	25.7	7.01	33.4
23	" " "	8	58.6	4.00	--	--	--	30.6	6.82	28.0
24	" " "	11	57.7	5.65	39.7	7.41	18.0	32.3	7.31	25.4
25	" " "	15	58.1	3.86	46.0	5.30	12.1	28.1	6.52	30.0
26	" " "	17	55.6	4.00	36.1	6.85	19.5	23.3	5.94	32.3
27	" " "	19	52.6	5.29	35.0	7.00	17.6	20.0	3.81	32.6
28	Dibutyl Phthalate	7	59.1	3.34	41.0	5.71	18.1	27.6	7.12	31.5
29	" "	8	57.2	3.86	45.0	6.23	12.2	36.0	6.81	21.2
30	" "	9	58.3	4.60	50.6	6.13	7.7	45.1	6.23	13.2
31	" "	10	55.9	6.34	39.1	7.01	16.8	33.7	6.88	22.2
32	" "	11	52.7	3.82	32.1	6.15	20.6	30.2	5.90	22.5
33	" "	12	49.3	3.74	30.8	4.91	18.5	11.5	2.97	37.8
34	Hercolyn	8			8.3			0.0		
35	"	10			12.0			0.0		
36	"	12			12.6			0.0		
37	"	15			17.1			5.0		
38	"	18			22.0			5.0		
39	"	20			26.6			--		
40	"	22			40.8			0.0		
41	"	25	50.4	6.82	44.0			35.5		
42	Untreated Strand	--	51.9	4.58	0.0			0.0

GRAPH III
AROCLOR.

GRAPH IV
DIBUTYL PHTHALATE.

ML. AROCLOR PER 100 ML. TORMESIT SOLUTION

ML. DIBUTYL PHTHALATE PER 100 ML. OF TORMESIT SOLUTION

GRAPH V
AROCLOR.

GRAPH VI
DIBUTYL PHTHALATE.

Further Investigation of Commercially Available Plasticisers.

Table 9 contains both the compositions of the solutions used, and the results of sea-immersion tests. Since the table is self-explanatory, the information contained therein is not duplicated here.

It is clear from the table that only two plasticisers deserve consideration, Aroclor No. 1242, and Dibutyl Phthalate. (Hercolyn appears very promising, but but the excessive concentration of plasticiser needed, together with the lack of desired flexibility of treated strands, would seem to eliminate it). A study of Graphs 3 and 4 reveal that both Aroclor and Dibutyl Phthalate exhibit optimum concentrations, and from these interpolated optima it is clear that Dibutyl Phthalate is more effective than is Aroclor.

Graphs 5 and 6 represent plots of the difference between the strengths of unimmersed strands and immersed strands, against concentrations of plasticiser. The interesting feature of these graphs is that they give optimum concentrations of plasticiser which agree exactly with those given by Graphs 3 and 4.

The optimum concentration of dibutyl phthalate, as read from Graphs 4 and 6, is 9 ml. of dibutyl phthalate per 100 ml. of Tornosit solution. Since the specific gravity of the Tornosit solution is approximately 0.95, 9 ml. of Dibutyl Phthalate per 100 ml. of Tornosit solution is equivalent to 11.4 ml. of dibutyl phthalate per 100 grams of benzene, a figure in almost exact agreement with that obtained from data on page (31).

Summary.

1. A new instrument for measuring flexibility of strands has been devised.

2. Several organic solvents have been shown to be without effect on the tensile strength of strands of 5/40 linen.

3. Gum chicle, gutta percha and pale crepe were chlorinated. Products containing various per cent. chlorine were obtained, by chlorinating for different periods of time, and at different temperatures. These products were used as preservatives on 5/40 linen twine. Tornesit, the commercially produced chlorinated rubber, was also tested, simultaneously. The tensile strengths of the treated strands, after several weeks immersion in the sea, showed all products from chlorination of gum chicle and gutta percha to be useless as preservatives, and the product from chlorination of pale crepe to be as effective, but not more so, than Tornesit.

4. The addition of a plasticiser to the chlorinated rubber is essential, in order that the treated strand have the necessary degree of flexibility. The tensile strength of a strand of 5/40 linen, impregnated with Tornesit plasticiser (dibutyl phthalate), is, after immersion in the sea for several weeks, a function of the concentration of plasticiser. An optimum concentration of plasticiser exists, at which concentration the life of a strand in the sea is greatest.

5. For all concentrations of Tornesit in benzene, and for all concentrations of plasticiser (dibutyl phthalate) of any practical value, no knot slippage occurs.

6. The most effective preservative found consists of an impregnating solution with the composition:

Tornesit (13 cps)	20 grams.
dibutyl phthalate	11 to 11.5 c.c.
benzene	100 grams.
copper napthenate	1 gram

stated more generally, the ratio of c.c. of dibutyl

phthalate to grams of Tornosit is 0.56 for 13 cps.
Tornosit. This ratio most probably applies to Tornosit
of viscosity 10 cps. to 20 cps.

Acknowledgments.

It is a pleasure to acknowledge the assistance given by the following: The Canadian Fishing Company, Vancouver, for the use of their tensile strength machine; the Physics Department of this University for constructing the flexibility apparatus; the Hercules Powder Company, Inc., Wilmington, Delaware, U.S.A., for furnishing samples of Tornesit.

Literature Cited.

O. "The Application of Plastics to the Development of a preservative for Fishing Gear".

R.V. Tyner and J.H. Fisher thesis submitted for the Degree of Master of Arts, in the Department of Chemistry, the University of British Columbia, April 1938.

BIBLIOGRAPHY.

1. Nancy Fleming and Aage Christian Thaysen. Biochem, J. 15, p. 25, 1920.
2. Charles Dorée. Biochem, J. Vol. 15, p. 709 - 1920.
3. A.C. Robertson, Ind. Eng. Chem. 23, 1093, 1931.
4. P. Waentig. "Über den Einfluss des Lichts auf Textilfasern". Zeitschrift für Angewandte Chemie, Band XXXVI, 1923, pp. 357-358, Leipzig.
5. Guy Barr and Isobel H. Hatfield, Dept. Sci. Ind. Research 2nd. Report Fabrics Coordinating Research Comm. 1930.
- 6.
- 7.
- 8.
9. "Properties and Values of Certain Fish-Net Preservatives". Harden F. Taylor and Arthur W. Wells, Bureau of Fisheries Document #947. Bureau of Fisheries, Dept. of Commerce, Washington, U.S.A.
10. See "The Chemistry of Synthetic Resins", by Ellis, Vol. 11, p. 1090, for numerous references to Staudinger's papers.
11. F. Kirchof, Gummi Ztg. 46, 497 (1932).
12. J. McGavack, Ind. Eng. Chem. 15, 961 (1932).
13. Francis C. Dyche Teague, U.S.P., 1, 826, 275, Oct. 6, 1932.
14. Herman Staudinger, German Patent No. 629, 453; April 30, 1936.

15. I.G. Farben industrie A-G, French Patent, 738, 434; Mar. 29, 1932.

16. M. Piolunkovskaya, J. Rubber Age (U.S.S.R.), 11, 142-9 (1934).

17. Douglas F. Twiss and John A. Wilson, British Patent 414, 862; Aug. 16, 1934.

18. New York Hamburger Gummiwaaren Compagnie French Patent; Nov. 4, 1931.

19. Douglas F. Twiss and John A. Wilson. British Patent 410, 249; May 17, 1934.

20. Soc. anon. des pneumatique Dunlop. French Patent, 766, 289; June 15, 1934.

21. Wilfred D. Spencer. British Patent, 402, 454; Dec. 4, 1933.

23. H.M. Broadhurst, A. Lambie, S.J. Peachey. British Patent, 127, 481; Sept. 19, 1918.

24. Carlton Ellis; U.S.P. 1,695,641; Dec. 18, 1929.

25. Imperial Chem. Ind. French Patent, 795, 196; Mar. 7, 1936.

26. Deutsche Gold-und Sieber Schneideanstalt vorm Roessler. French Patent, 787, 354; Sept. 21, 1935.

27. I.G. Farbenind A-G. British Patent, 382, 154; Nov. 10, 1932.

28. Private Communication; Hercules Powder Co., Ind. Wilmington, Delaware, U.S.A.

29. F.J. Peters; Z. Ver. Deut. Ing., 80, 1469-74 (1936).

30. Douglas F. Twiss, John A. Wilson, British Patent 410, 249. May 17, 1934.

31. Francis C.D. Teague. British Patent 462, 008. Mar. 1, 1939.

32. "The Chemistry of Synthetic Resins" Carleton Ellis, Vol. 11, p. 1118.