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A SURVEY OF PUBLICATIONS

DEALING WITH CORROSION IN WIRE ROPE

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by

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DEPARTMENT OF CIVIL AND MECHANICAL ENGINEERING

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A research of the literature (both the journal literature and the report literature) was conducted to collect all work dealing with the corrosion and prevention of corrosion of wire rope. A discussion of the various types of corrosion, cathodic protection, coatings, and lubricants is given along with references for these topics. Forty-one references are included.

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DEALING WITH CORROSION IN WIRE ROPE

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A. Introduction

Wire rope is an exceedingly complex piece of hardware, it is composed of a large number of cold drawn wires wound together into strands which are themselves wound together to form the wire rope. The inherent stresses that each wire contains after the forming process is completed is impossible to even imagine. The free space left between wires and strands is constantly changing as the rope flexes in use. This flexing also causes the wires to rub against one another so that any corrosion products on the wires, which normally provide protection, are removed and the bare metal surface exposed. A system more susceptible to corrosion probably could not have been designed. And yet wire rope is one of the most indispensible pieces of equipment used in the ocean today. It is the best that is available for the jobs that must be done. This, added to the fact that it is not cheap, makes it imperative that its lifetime be extended as long as possible. Since corrosion is one of the most common causes of wire rope failure, it is important that as much as possible be known about the corrosive interaction of salt water and wire rope.

In this report we shall deal exclusively with the corrosion and the prevention of corrosion of wire ropes. The first section will be devoted to a discussion of the various "types" of corrosion phenomena which have been observed to occur in wire rope. In each case a short discription of the corrosion process itself will be given and then a discussion of the situations in which this type of corrosion was observed in wire rope. The second section of the report deals with cathodic protection and its use as a preventor of corrosion in wire rope. Also in this section there will be a discussion of situations in which cathodic protection has been used for wire rope and the results of such applications. Finally, the last section deals with various types of coatings and lubricants that have been used in order to lessen the corrosive effect of sea water. To complete these discussions a listing of references dealing with the corrosion and the prevention of corrosion of wire rope is presented.

A topical index has also been included to aid the reader in using this report. The author found it convenient in preparing this report to computerize the retrival of information from these and other references. A copy of the retrival program and has also been included.

In any survey of this type, it is inevitable that some work will be overlooked. The author would encourage any reader of this review to communicate to him any ommissions.

B. Corrosion

Before examining the various special types of corrosion processes it may be profitable to give a general background into the corrosion process itself. As a general text which covers both the theory and a wide range of engineering practice concerned with corrosion, reference 10 is recommended.

The corrosion of metals in a conducting fluid medium is an electrochemical phenomenon. At one location on the metal surface the atoms lose electrons and become anions. The electrons remain in the metal; the ions, which are soluble, enter the liquid phase. The electrons which were left in the metal flow to another spot on the metal surface and are there taken up by some cation in the liquid phase. At the spot where the metal ions were produced, at the expense of the metal, the metal is said to have corroded. In electrochemical terms this area acted as an anode. The location where the electrons were taken up by the cation is said to act as a cathode. The chemical reactions involved are represented by the equations

$$M = M^{+n} + ne^- \qquad \text{(at the anode)}$$

$$O_2 + 2H_2O + 4e^- = 4OH^- \qquad \text{(at the cathode)}$$

Notice that corrosion does not necessarily take place at the same spot where oxygen is present. This will be discussed more fully in the section dealing with crevice corrosion.

While the above is a very simple explaination of the corrosion process, other factors tend to complicate the situation and lead to a variety of special cases of corrosion, each of which bears a different name. Practically all of these special cases are exhibited by wire rope. In the next few subsections those cases that do occur for wire rope will be discussed from two viewpoints. First, from a general discussion of that type of corrosion, and second, cases in which this type of corrosion has been reported for wire rope.

1. Uniform Corrosion

Uniform corrosion is said to occur when the entire piece of metal corrodes away more or less uniformly. Wire rope, when used in the ocean, is usually of such a length that this type of corrosion does not occur. Locally, however, it does occur for individual strands and over short lengths of the rope.

The mechanism for this type of corrosion is as follows: the entire surface behaves as an anode and begins to corrode. As the corrosion products are formed they react with the cations in the sea water and these products, chiefly hydroxides of the metal, cling to the wire rope and change its electrochemical character. This area may, in turn, act as a cathode and the previously cathodic area may act as an anode and corrode. The surface of the wire rope will become discolored, reduced in dimensions, and otherwise changed in appearance. All wire ropes unless they are cathodically protected, take on this appearance.

2. Crevice Corrosion

Crevice corrosion is a local effect and, as the name suggests, occurs in crevices and other areas where the water is allowed to remain stagnant. It occurs sufficiently often under gaskets to have earned the name gasket corrosion.

In the general discussion earlier in this report it was pointed out that the corrosion reaction need not take place in that part of the system which contains oxygen. It is only necessary that the electrons released into the metal "find" the oxygen at some other place on the surface. Crevice corrosion takes this phenomena to the extreme limit. It is best illustrated by two figures. Figures 1 and 2 represent a piece of wire rope. Half of the rope is covered by tape. Figure 1 represents the initial stage of the process. That is, at some time when the composition of the water under the tape and in the main body of the sea is the same. In Figure 1 it can be seen that the corrosive action is the same in the area covered by tape as it is in the area not covered. In both cases the metal is corroding and oxygen is being reduced to hydroxyl ion. As time goes on, however, the oxygen will be depleted in the area under the tape since the corrosion reaction takes place faster than the oxygen can diffuse through the water under the tape. This has two effects on the corrosion process. First, when a metal ion is produced under the tape the electron must travel through the wire rope to an area not under the tape to find an oxygen molecule to reduce. Second, continued corrosion under the tape tends to produce a surplus of positive charge in that area. To offset this and to produce an electically neutral solution there is a general diffusion of negative ions from the area not under the tape to the area under the tape. Since the chloride ion is the predominate negative ion in sea water it is this ion which diffuses under the tape. The relatively high concentration of the metal ion in the tape covered area leads

to the precipation of the metal ion as the metal hydroxide, $M(OH)_n$. This tends to increase the acidity of the water under the tape. It is this combination of acidity inthe presence if chloride ion which greatly increases the corrosive effect under the tape. This state of the wire rope is shown in Figure 2 which represents the wire rope at a later time in its history.

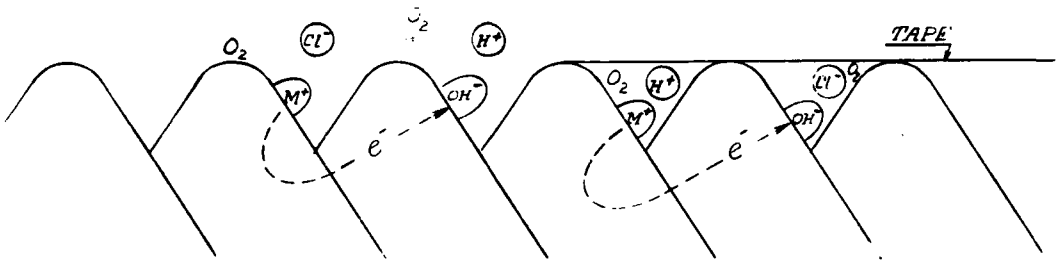

Figure 1

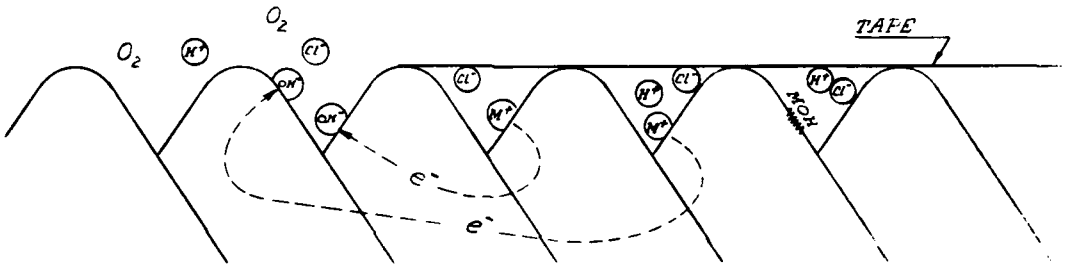

Figure 2

As the corrosion in the "crevice" increases, the electrons provided to the untaped area serve to protect this area from corrosion. This form of cathodic protection is not to be desired.

Because of the stranded nature of wire rope, fittings, tape, and other coverings only touch the ridges of the strands. Thus the valleys between the strands act as areas in which crevice corrosion can take place. In particular, this phenomena is reported in references 19 and 18 in conjunction with taped areas of wire rope. Reference 13 reports a very severe case of this type of corrosion for a 304 stainless steel wire rope covered with a neoprene jacket. It is also stated in this reference that under stainless steel fittings the 304 stainless steel rope corroded in a pattern which was an imprint of the fitting.

A second type of crevice corrosion makes use of the naturally occuring crevices that exist between the individual wires themselves. It then takes the appearance of a dimunuation of the diameter of the wires. In wire rope work this form of corrosion is also called "necking down". In severe cases the wire eventually breaks and the ends spring out of the wire rope producing "fish hooks".

This type of corrosion occurs practically every time that wire rope corrodes. Some very graphic photographs of this phenomena may be found in references 6, 13, and 19. Reference 6 reports that improved plow steel, galvanized,and stainless steel rope exhibited both necking down and fishhooks. Phosphor bronze [18], after 183 days of total immersion, exhibited considerable necking down. Some wire ropes made of relatively exotic materials like monel [6], nickel base alloys, copper-nickel clad stainless steels (types 304L and 205), and titanium [18] show little or no necking down in tests lasting 41 weeks (for monel) and 790 days (for the others).

Finally, crevice corrosion can occur in a single wire. In this case the stagnant region is not covered but relies on the absence of mechanical disturbances strong enough to flush the oxygen poor water out of the crevice. A very striking example of this is reported in reference 18. In this study 90/10 copper-nickel clad stainless steel (types 304L and 205) ropes were immersed in sea water for 790 days. At the end of that time both clad and unclad ropes had many individual wires which exhibited crevice corrosion. Some of the wires were so badly corroded that they were actually hollow cylinders at the end of the experiment. The walls of the "cylinders" were thin enough to be pierced by a needle even though they appeared to be unharmed.

Some photographs of "normal" crevice corrosion of individual wires can be found in reference 20. It should be noticed that both inner and outer wires were subject to this type of corrosion.

3. Pitting Corrosion

Pitting corrosion is an extremely localized form of crevice corrosion. The mechanism is exactly the same once the process begins, the inside of the pit acting as the crevice. The mechanism by which the process begins, however, for a given piece of metal is still unknown. For a wire rope the crevices between the strands and wires provide a starting point just as they did for

crevice corrosion. The question as to why the corrosion follows the form of the crevice in some cases and develops a pit in others is a puzzling one. The answer probably lies in the crystal structure [10] of the metal at that particular point. Of the two types of corrosion, pitting is the most dangerous because the attack is extremely localized and weakens the wire rope considerably in a very short time.

Pitting has been observed in practically every type of wire rope. In reference 4 it is reported that ropes made from titanium and some of its alloys resisted this form of attack. Stainless steel wire ropes appear to be particularly susceptible to pitting and a very interesting picture of this is shown in reference 6. It is very clear from this picture that the starting point for the pit was in the crevice between the individual wires. Reference 18 also reports a pitting attack on stainless steel. In general, resistance to pitting for wire rope materials seems to follow the same trend for these materials used in other applications [10].

As in the case of crevice corrosion individual wires can also be attacked. Reference 20 contains photographs which show this type of attack on type 304 stainless steel on both outer and inner wires.

C. Cathodic protection.

The most successful method now available to prevent the corrosion of wire rope is cathodic protection. Although a great deal of work has been done in measuring the effectiveness of this method it has only been used a few times in working wire rope systems. With the increased demand for long term deep sea mooring stations and scientific package implacements, it seems clear that cathodic protection of wire rope is going to be an increasingly important subject.

It is important to emphasize that cathodic protection can protect wire rope. It is equally important to point out that it is expensive and needs periodic maintenance which is not convenient to do in very deep water. The expense and the frequency of the maintenance can be reduced if the rope is protected by other means also; for example, by coatings of grease or other corrosion resisting substances. Thus, cathodic protection should be looked upon as a method which should be used in conjunction with other methods.

1. Theory

Cathodic protection takes advantage of the fact that corrosion is an electochemical process. In section B of this report it was stated that the corrosion process involves the reactions

$$M = M^{+n} + ne^-$$
$$O_2 + 2H_2O + 4e^- = 4OH^-$$

where the first reaction is the one that destroys the metal. The reaction takes place because of a difference in potential between the anodic and cathodic portions of the metal. The first reaction can be prevented if the wire rope can be driven to a lower potential. This can be done by attaching to a wire rope a piece of more active metal or by using an independent electrical source to provide the potential. In the latter case an inert electrode (usually graphite) is used to complete the circuit. Figures 3a and 3b show schmatically the two types of protection.

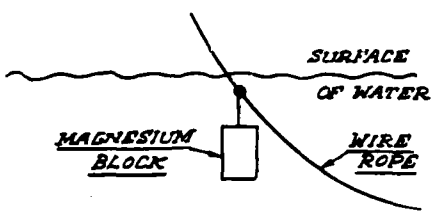

Figure 3a

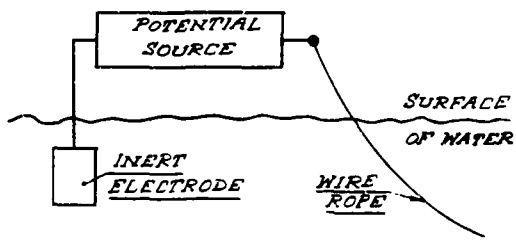

Figure 3b

The method which uses the more active metal is commonly the sacrificial anode method. The chemical reactions that take place are

$$M = M^{+n} + ne^- \quad \text{(on the sacrificial anode)}$$
$$2H^+ + 2e^- = H_{2(gas)} \quad \text{(on the wire rope)}$$

The net result is that the more active metal corrodes away and in doing so provides the wire rope with electrons which reduce hydrogen ions in the sea water to hydrogen gas. Thus, this method requires the periodic replacement of the sacrificial anode.

The second method is called the impressed current method. In applications other than wire rope this method is widely used. The major obstacle in its use for wire rope systems is that the systems are usually located in areas where electrical power is not readily available, e.g. the Gulf of Mexico. The current densities that are required and the long lengths of wire rope to be protected make the use of batteries impractical.

In order to provide adequate cathodic protection to a wire rope, three things must be known: (1) the location on the wire rope at which the protecting potential should be applied, (2) the strength of the applied potential, and (3) the effective lifetime of the system chosen to provide the potential. Each of these questions must be answered by a different discipline: the first by thermodynamics (where will the system have the greatest driving force to corrode?); the second by transport theory (what potential and current should be applied to the wire rope to protect the greatest length of rope?); and the third by electrochemical kinetics (how rapidly will the applied current be used in protecting the wire rope?).

It has been shown, both experimentally and theoretically [33], that areas of high stress tend to corrode preferentially over areas of lesser stress. Thus, in wire rope systems the cathodic protection should be (and is) applied at a point where the stress is the greatest.

The second question has been investigated experimentally [6,7,27] based on an empirical relationship developed for the cathodic protection of underground pipelines. A more rigorous theory has recently been put forward [32] which substantiates the empirical formulae. Both theory and experiment show that a given potential will only protect a fixed length of wire rope. Increasing the potential is impractical for the sacrificial anode method since each individual metal has a fixed potential in relationship to a given wire rope material and high potential materials are prohibitively expensive. The materials in common use now are zinc, magnesium, and sometimes aluminum. Increasing the potential using the impressed potential method is inefficient because most of the additional current provided goes into more vigorous hydrogen evolution near the anode [7]. The increase in the length of wire rope protected is not worth the increased cost. The answer to this dilemma seems to be to place more than one source of protecting potential on the same wire rope [7,27,28,29] at some prescribed distance apart.

There has been essentially no work done in the third area.

2. Testing

The number of tests that have been conducted on the cathodic protection or wire ropes is indeed legion. Undoubtedly the first such experiment was performed by Sir Humphrey Davy [8]. While conducting experiments on the cathodic protection of copper, he used about 40 feet of copper wire protected by a zinc electrode and found no diminution with length. Subsequent experiments have shown this to be incorrect. Rather than attempt a review of the literature of the specific types of wire ropes, both from a material point of view and from a construction point of view, the reader is referred to the index of this report. A few general remarks can be made however. Cathodic protection tests have been conducted on virtually every type of wire rope, ranging from ordinary plow steel to relatively exotic materials like monel. Furthermore, ropes of all sizes and construction have been tested with the general conclusion that fiber core wire rope is actually adversely affected by cathodic protection because the fiber core is eaten away by the increased alkalinity of the water inside the cathodically protected wire rope. Also, testing has been performed on ropes that were completely submerged, in the mud, and exposed to the splash region of the sea.

3. Applications

Two major wire rope systems utilizing cathodic have been sufficiently documented to be included in this report. The first was the Tongue of the Ocean Deep Sea Moor (called AUTEC TOTO II) and the second was the NOMAD Buoy Mooring System.

The TOTO moor was an extremely ambitious project to provide a deep sea mooring capability. Unfortunately, the question of cathodic protection appears not to have arisen until after the moor was designed, [27,28,29]. Even so, a cathodic protection system was developed and used. One partial replacement of the anodes took place after three and one half years. However, the moor failed after four and one half years of service. A post-mortem was conducted and a conference report [27] published. A detailed discussion of the failure of the moor and the performance of the cathodic protection system is given in reference 13. The opinion expressed in the conference report and in reference 13 was that the cathodic protection system did all it was supposed to do, but other factors (the fact that it came into the

design phase late, a lack of monitoring of the condition of the sacrificial anodes, and improper replacement techniques) prevented its full potential from being exploited.

The NOMAD system [20] was recovered before failure after 34 months in the Gulf of Mexico. The analysis of the performance of the cathodic protection system in reference 20 is excellent.

D. Coatings

In the preceeding section of this report a method of corrosion prevention was discussed which was basically a trade off method. That is, a non-load bearing part of the system (the sacrificial anode) was allowed to corrode in order to prevent the corrosion of the working part of the system. In this section the discussion will center around the problem of modifying the surface of the wire rope itself so that it becomes more corrosion resistant. These modifications shall be called by the general term "coatings". In this report coatings will be divided into three groups : metallic, plastic, and lubricants.

1. Metallic

Wire rope is said to be "clad" if it is coated with a metal different from that which the wire rope is constructed. This coating is applied to the individual wires themselves before the wire rope is constructed. In almost every case the wire rope is clad with a more active metal (an exception to this is found in references 3 and 14 in which lead and copper coated stainless steel and high nickel alloy wires are discussed). This has the advantage that the more active metal provides cathodic protection to any portion of the metal from which the wire rope is constructed in the event that the coating is damaged by corrosion or wear.

The most commonly used metals for coating a wire rope are zinc and aluminum. In the former case the rope is said to be galvanized; in the latter case it is said to be aluminized. Both corrode more slowly than high carbon steel primarily because the corrosion products tend to be more tightly held on the surface than those of steel. Aluminum is superior to zinc in this respect [1, 16, 34]. Zinc, on the other hand, is better at providing cathodic protection because the corrosion products on aluminum are too tightly held and fresh aluminum cannot be exposed to complete the electrochemical cell (for an example of the effectiveness of zinc clad wire rope see reference 15).

Quite a bit of work has been done on the effectiveness of metallic coatings in prolonging the life of wire rope. Usually the wire rope was cathodically protected at the same time. Pictures of the cross section of some galvanized wire ropes may be found in references 13, 19, and 27. These pictures show the pattern of the remaining zinc after a period of corrosion. As might be expected the zinc on the outer wires had been corroded away completely while the inner wires retained a good portion of their coating. In some cases the use of materials which are not sufficiently more active than the material from which the wire rope is constructed can lead to rather severe problems. An example of this was discussed in the section on crevice corrosion in connection with some copper-nickel clad stainless steel wire rope. The reason seems to be that the cathodic protection offered by the coating is not sufficient to overcome the electrochemical potentials developed during the crevice corrosion process.

Probably the most serious threat to the coating is not corrosion but wear that occurs when the wire rope is in contact with those devices which are used to handle the wire rope (like sheaves, rollers, etc.). References 15 and 27 describe cases where there was considerable damage to the coating for both zinc and aluminum clad rope.

Finally, it should be pointed out that there is some disagreement in the literature concerning the relative strength of clad versus unclad wire rope. The Roebling Wire Rope Handbook (35) states that the "listed strength" (meaning the breaking strength) of galvanized wire rope is 10% less than the same rope which is unclad. This is also mentioned in reference 27 for both aluminum and zinc clad rope. Reference 34 states, however, that aluminum clad rope has the same strength as a non-clad rope.

2. Plastic

Plastic coatings of wire rope range from jackets that cover an entire wire rope to "spaghetti" type coverings of the individual wires. This is an area in which a great deal of work is now being done. The materials used must be flexible, fatigue resistant, have a low permeability to sea water, and resist fish bite. Their greatest drawback lies in the fact that if a break in the coating occurs very severe crevice corrosion will result. This will also be true if the material has an appreciable permeability with respect to sea water.

The jacket type of covering has been used in sea water as part of a working system [20]. Two hundred feet of 304 stainless steel wire rope (out of a total

of 1250 feet) was covered with a neoprene jacket primarily to prevent abrasion of some synthetic rope used nearby. Serious crevice corrosion was observed (after 34 months exposure) to have occurred under the neoprene even though the wire rope was cathodically protected. A second test [26], which used a plastic (unspecified) jacket over a galvanized wire rope showed some corrosion after 13 months. Before this method can be recommended for general usage, it seems clear that more study is necessary.

Individual plastic coated wires have been tested many times [3,17,25,26], and shown to be quite resistant to corrosion. As far as could be ascertained however, no wire rope made up of individual wires, all plastic coated, has ever been tested.

3. Lubricants

Lubricants serve a dual purpose. They cut down on the wire-to-wire abrasion and the rope-to-fixture abrasion and also play an important roll in the prevention of corrosion. The lubricants themselves are generally petroleum products (oils, waxes, and asphalts) or soaps [3] with additives that are termed corrosion inhibitors. In the manufacture of the wire rope, or in shops, where the wire rope can be heated, higher viscosity materials can be used to coat the individual wires and fill the void spaces between strands [35]. For service in the area of use this type of application is usually not feasible so low viscosity oils are available and standard procedures have been developed, along with the necessary equipment [35], to apply them. The purpose of these low viscosity materials is to flow into the void spaces and provide the necessary lubrication. Greases are also available [41] to serve as coatings of the wire rope. In general, the topic of lubrication seems to be an area where whatever available is used, provided it meets the minimum specifications of the user.

E. Sources

A number of different types of sources were consulted to obtain information on the corrosion of wire rope. These included:

1. Abstracting services
   a. Chemical Abstracts - 1907 to Nov. 7, 1970
   b. Corrosion Abstracts - 1962 to Nov. 1970

2. Survey reports

a. A Survey of Publications on Mechanical Wire Rope and Wire Systems, H.H. Vanderveldt and R. de Young, Report 70-8, Institute of Ocean Science and Engineering, Catholic University of America, Washington, D. C. 20017, (1970)

b. A Bibliography of Wire Rope Literature, Lab Project 9300-44, Technical Memorandum 2, U.S. Naval Applied Science Laboratory, Brooklyn, New York, (1969)

3. Government Laboratories

a. Naval Research Laboratory, Washington, D. C. This laboratory has done a great deal of work on the cathodic protection of wire rope and they graciously provided copies of their memoranda on this subject.

b. Naval Ships Engineering Center, Prince Georges Center, Hyattsville, Maryland 20782.

F. Retrieval Computer Program

In the process of collecting the references and writing this report it became convenient to program a retrieval procedure for easy recall of the various topics of interest. At the same time it was decided to include other topics which might be of interest in the future. This latter consideration makes the following program more general than necessary for this report but still applicable.

The "comment" cards of the program describe its operation and the format of the data cards. A data card is divided in three parts. Columns 1 through 6 contain the number of that particular card, right justified. Columns 40 and 41 contain the last two digits of the year the reference appeared. All of the rest of the columns are available for a topical index. If the reference involves that topic, a 1 is punched in the appropriate column. Otherwise, the column is left blank.

The control of the search of the bibliography available is the logical IF statement immediately preceeding statement number 5. If the data card has "ones" in all the columns specified, that card is "recalled". This is accomplished by printing the number of that card. The paper associated with tht number can then be "retrieved" from the collection of papers.

For illustrative purposes the program is set up to recall those papers involving the use of cathodic protection in sea water.

```
C    DATA CARD CODE
C    COLUMNS 1-6 ARE RESERVED FOR K, THE DATA CARD NUMBER
C    COLUMNS 8-19 ARE RESERVED FOR THE TOPICS LISTED BELOW
C    8    SEA WATER
C    9    WIRE ROPE
C    10    CATHODIC PROTECTION
C    11    ANODIC PROTECTION
C    12    STEEL OR IRON
C    13    WIRE
C    14    SHIPS
C    15    BIOLOGICAL ACTIVITY
C    16    MAGNESIUM
C    17    COPPER
C    18    STRESSED
C    19    PROTECTIVE COATINGS
C    COLUMNS 40-41 ARE RESERVED FOR THE LAST TWO DIGITS OF THE YEAR
C    COLUMNS 7,20-39,AND 42-80 ARE BLANK
      DIMENSION J8(200),J9(200),J10(200),J11(200),J12(200),J13(200),J14(
     1200),J15(200),J16(200),J17(200),J18(200),J19(200),YEAR(200)
      INTEGER YEAR
C    M IS THE EXACT NUMBER OF DATA CARDS
      READ(2,100)M
  100 FORMAT(I3)
      WRITE(3,1000)
C    FORMAT NUMBER 1000 WRITES THE TITLE/TITLES OF THE TOPICS TO BE SEARCHED FOR
C    START NEW PAGE WITH THIS FORMAT STATEMENT
 1000 FORMAT(1H1,53HTHOSE PERTAINING TO CATHODIC PROTECTION AND SEA WATE
     1R)
      DO 3 I=1,M
    3 READ(2,1)K,J8(K),J9(K),J10(K),J11(K),J12(K),J13(K),J14(K),J15(K),J
     116(K),J17(K),J18(K),J19(K),YEAR(K)
    1 FORMAT(I6,1X,12I1,20X,I2)
      DO 7 K=1,M
C  THE  FOLLOWING CARD CONTROLS THE SEARCH
      IF(J8(K).EQ.1.AND.J10(K).EQ.1)WRITE (3,5)K
    5 FORMAT(1X,I6)
    7 CONTINUE
      CALL EXIT
      END
```

G. Acknowledgement

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II. Bibliography

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