Evaluation and Uses of Organic Inhibitors

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Organic inhibitors have been used in many applications but probably most extensively in the petroleum industry. In general, they may be divided into two groups. One group may be classed as "rust inhibitors" insofar as their primary purpose are to inhibit against attack by oxygen. The other group, as used to prevent corrosion in producing oil and gas wells and in the refinement of oil, are made to be effective in the prevention of attack by acids such as hydrogen sulfide, carbon dioxide, hydrochloric acid, acetic and propionic acids, and the like.

Prevention of corrosion in this last class is probably the most difficult. The reason for this is that the environment in which corrosion occurs is not a simple one. Invariably multi-phase systems are encountered composed of oil, water, and gas under wide ranges of pressure and temperature and these phases will vary quite widely in composition. Water encountered varies widely in dissolved salt concentrations and in amount. Similarly the composition of the oil may vary from light paraffins, such as propane and butane, to the heavy waxes and asphalts. The oil may contain natural occurring polar substances such as organic acids, phenols, ketones, and organic bases (1), (2) which may cause partial wetting of the oil. This partial wetting in a two phase system may completely discredit expected chemical reaction behavior of a single phase system.

The structure of an organic inhibitor has been compared by many persons to the shape of a tadpole. The head is analogous to the polar end of the molecule which normally contains one or more of the elements of sulphur, nitrogen, or oxygen in some form. The tail of the molecule is usually a hydrocarbon residue of some structure to provide oil solubility to the molecule.

It is believed by most researchers that these molecules are generally adsorbed in monolayers over polar surfaces, such as metals, as described by Langmuir and Schaefer.(3) The polar end is adsorbed at the solid interface leaving the non-polar oil-soluble end migrating out from the surface. The effect is the formation of a film formed over the surface to present a substantial energy barrier from penetrating corrosion molecules.

There are certain properties which these inhibitors must possess. They must be compatible with agents present in their environment. For example, most oil field waters contain dissolved salts of calcium, magnesium, sodium, etc., and an inhibitor should not react to form soaps or other insoluble compounds. An inhibitor should be soluble to the degree that it will be dispersed into at least one phase. Preferably it should be distributed into all phases.

Also, the inhibitor should have a fast adsorption rate and a slow desorption rate resulting in long film life. It, also, should be sterically constructed so that the molecules adsorb together closely packed to form a continuous film.

EVALUATION OF INHIBITORS

Laboratory Results

The primary difficulty in evaluating inhibitors in the laboratory is the inability of the researcher to exactly duplicate field conditions. Field conditions, in turn, vary

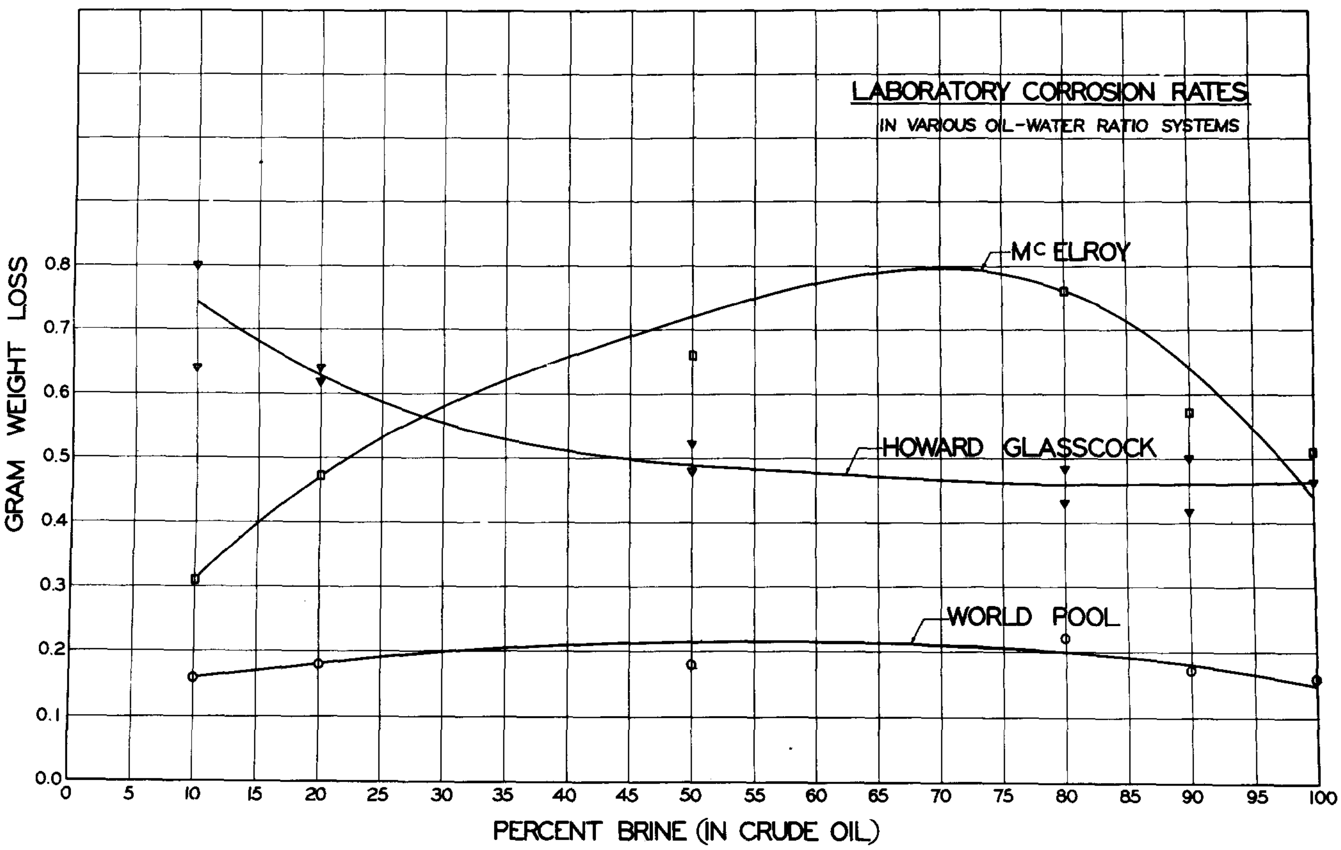


Figure 1

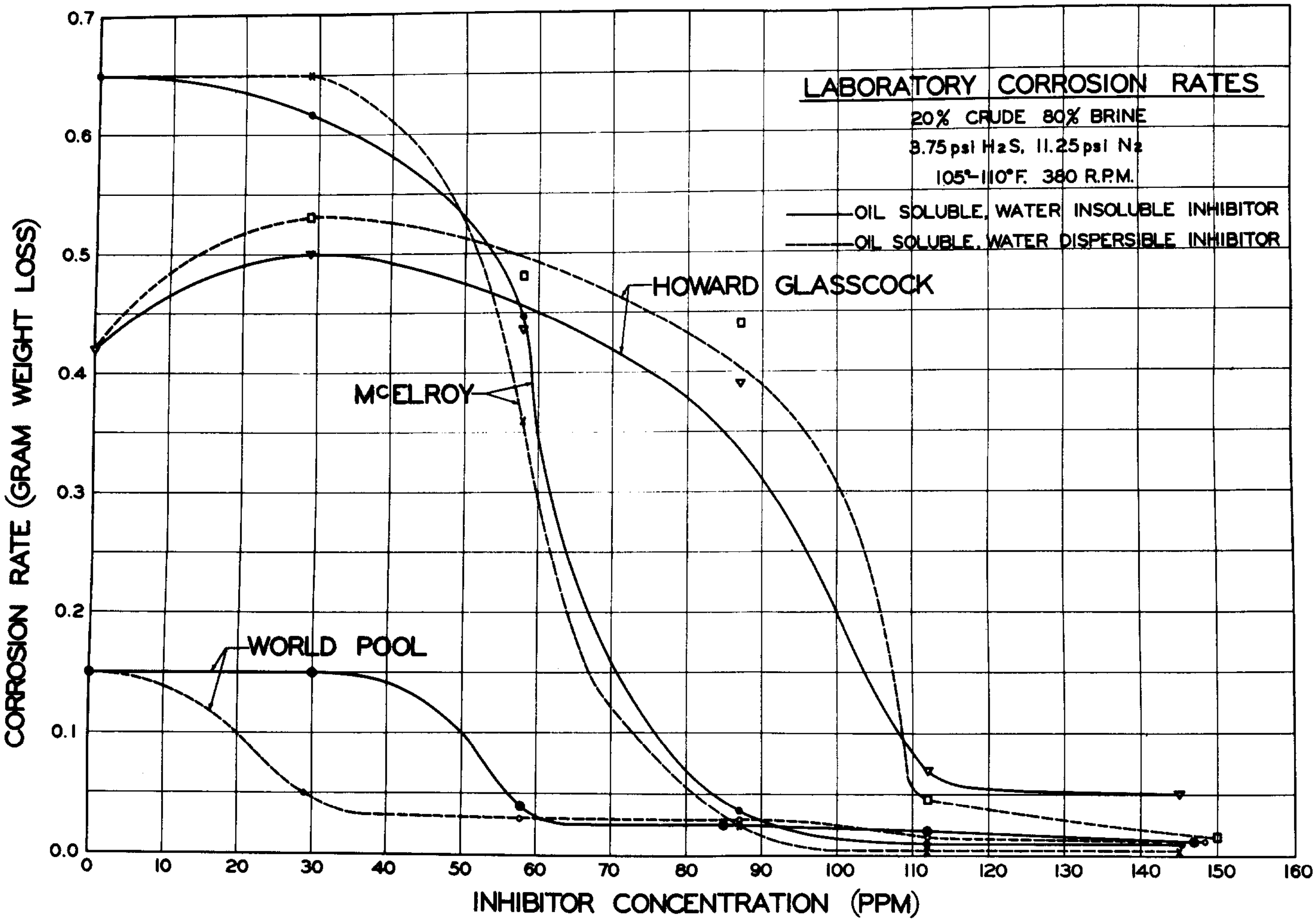


Figure 2

widely as do the corrosion problems vary in cause, effect, location, and magnitude. For this reason no single laboratory test involving the use of a standard water or oil can be used to evaluate a corrosive condition or the expected performance of an inhibitor.

Figure 1 illustrates how the variances of oil/water ratios effect corrosion rate. Figure 2 illustrates how inhibitors vary in different oils and waters and at one oil/water ratio. All oils and waters, being of widely varied composition, cannot be expected to behave similarly. Also, other factors such as temperature, pressure, velocity, pH, composition of both oil and water, play an important part. (4)

There are a number of methods available for evaluating organic inhibitors. Greco and Spaulding describe some of these in a paper entitled "Laboratory Methods for the Evaluation of Inhibitors for Use in Oil and Gas Wells". (5)

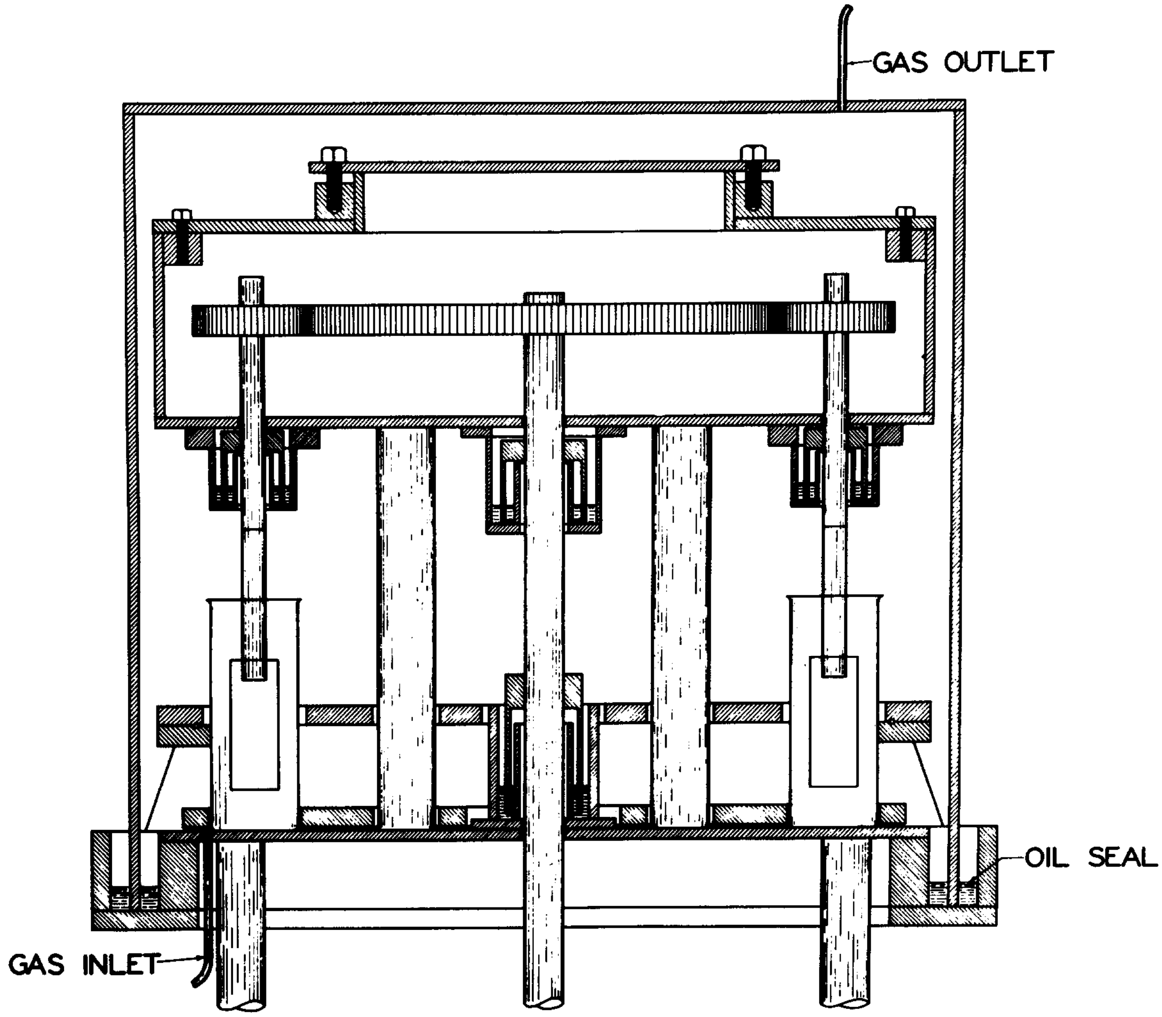
The most popular tests involve the use of actual well fluids in a so-called "stirring test." Usually weighed coupons are stirred in well fluids at controlled temperature, velocity, and under a controlled atmosphere of gases usually containing H_2S and/or CO_2 for a specific period of time (Fig. 3)

Another method involves the separate pumping of oil, water, and inhibitor into a cell containing a metal strip under controlled conditions. In this test hydrogen evolved by the corrosion process is read on a thermal conductivity cell and results are plotted as the inhibitor is added. This method has the advantage over the batch test insofar as continuous data are available and studies of desorption rates or film life can be determined. Figure 4 illustrates some data obtained by this procedure. Similar data may be obtained by the classical adsorption studies as illustrated in Figure 5.

The NACE has adopted a screening test for inhibitors (Fig. 6). This test is relatively simple in that the inhibitors are tested at a concentration of 10, 25, 50, and 100 parts per million based upon the total amount of fluid. The total fluid in the flask consists of 900 milliliters of brine and 100 milliliters of oil, or a total of 1000 milliliters. First the flask is purged with prepurified nitrogen and oil and is placed in the bottom of the flask. Brine is introduced to the bottom of the flask slowly to avoid splashing. If an oil soluble inhibitor is used, it is added directly to the flask. When the system is completed as above, a weighed coupon measuring 1" x 1" 1/16" is suspended on a glass rod in the oil phase for 10 seconds. It is then extended into the brine where it is allowed to remain for seven days. At the end of this time the coupon is removed, cleaned electrolytically or by means of inhibited acid until free of corrosion products. The coupon is then weighed and the corrosion rate determined.

The test has the disadvantage of being a static test which may tend to give erroneous results in some instances. It is only meant for screening purposes so, hence, the test may have value of qualitative purposes but certainly not for quantitative answers.

The governments of both the United States and Canada, as well as other countries, have recently stipulated that aircraft fuels must contain an oil soluble corrosion inhibitor. Inhibitors are evaluated by a modification of the ASTM turbine oil test D-665. This test involves the stirring, for a specific period of time, of fuel containing 10% water into which a polished metal rod is suspended. The degree of rusting of uninhibited fuels are compared with fuels containing various amounts of inhibitor.



HALF SECTION
CORROSION TEST APPARATUS

Figure 3

Field Evaluation

Field evaluation of inhibitors strangely are usually laborious. This results from the fact that it is extremely difficult and usually impossible to measure directly the corrosion rate at the point of actual attack. Also, corrosion may be localized or may be slowly progressing so that a long period of time is required. There are, however, several tests that can be utilized to estimate corrosion and results of treatment.

Iron Contents Test

It is reasoned that as metals corrode, the environment should become contaminated with the metal corrosion product. Therefore, many operators take samples of the well fluids at the surface and analyze for iron content. In gas condensate wells this method is most useful because usually all components are above the critical temperature at the bottom of the well, and are, therefore, in the vapor state. In this case, all iron present at the well head are a result of corrosion. A comparison of iron before and after treatment gives a good indication of the effectiveness of treatment.

In the case of pumping and flowing wells producing formation water, the results may not be so significant as the formation water may contain natural occurring iron. It is, therefore, difficult to distinguish between natural occurring iron and iron corrosion products. Also, if the well produces a large quantity of water and if corrosion is localized, a very small change in iron may be quite significant. Many times this small change is not within the experimental error or range of the analytical method. If the well fluids contain hydrogen sulfide, the iron will be present as insoluble iron sulfide. This makes it difficult to obtain a representative sample and all the results must be reviewed with skepticism.

Test Metal Coupon Specimens

Many individuals use a method of installing weighed metal strips placed in the corrosive environment. Usually these are fabricated from cold-rolled 1020 mild steel, 16 gauge, and are approximately 1-in. in width by approximately 5-in. in length. The surfaces may be either polished to a specified finish or sand-blasted. The normal exposure is for 14 days after which time they are cleaned and reweighed and a calculation for corrosion rate is made. Comparisons are made after inhibition with that prior to treatment.

This method has the disadvantage that it only gives an indication of corrosion rate at the point of exposure. Unfortunately, usually this point is not where corrosion is a problem as this is usually on subsurface equipment thousands of feet below the well head. Many times no corrosion is observed at the surface.

In a majority of cases, test coupons can be used to good advantage in at least establishing a trend of actual corrosion conditions. They are useful in regulating the amount of inhibitor used to control corrosion, particularly if data are taken over long periods of time and are compared with actual well replacement records.

Pony Rods

In evaluating corrosion in pumping wells, many operators have used the so-called "pony rod" method of evaluation. In this case, short rods, usually 4 foot in length, are sand-blasted and weighed and installed in the rod string of the well. Usually a rod is placed immediately above the pump and another rod is placed nearer the well head. These rods are normally left in for a period of approximately 3 months. The disadvantage of this method is that it is costly to remove the rod and that the time between the periods of examination are long. It has the advantage that the actual corrosion rate on the rod can be observed at the point where corrosion is the problem.

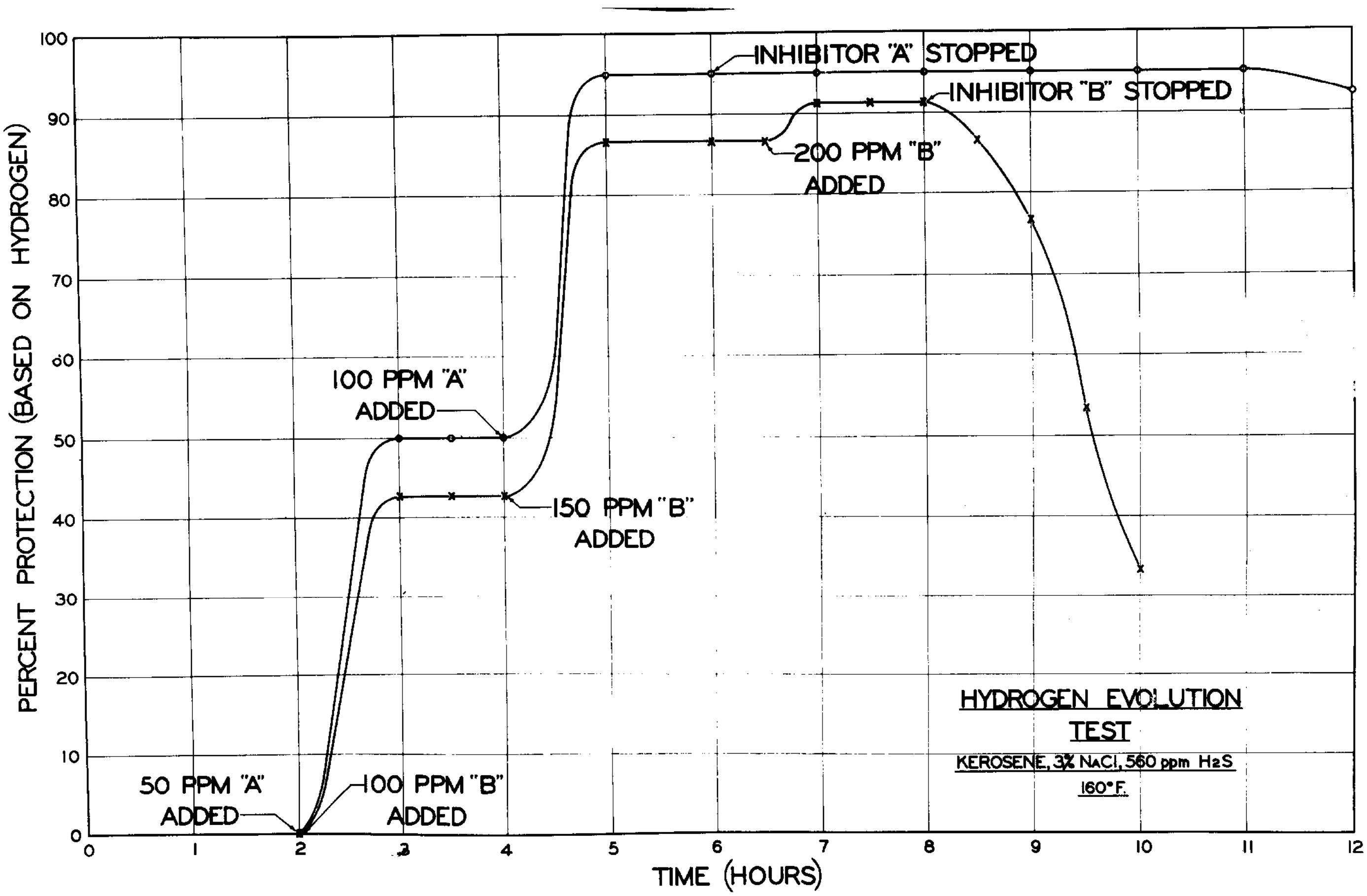


Figure 4

Caliper Surveys

Another method used for determining corrosion rate on the internal surfaces of tubing is through the use of the Tubing Caliper. This tool is lowered by means of a line to the bottom of the well. As the tool is retrieved, actuated feelers literally feel for corroded pits. A stylus records these pits as a permanent record as the tool moves up through the tubing.

This method has the advantage of inspection without removing the tubing from the well. It is, however, somewhat expensive and cannot be used if there are any obstructions in the tubing string.

USES OF ORGANIC INHIBITORS

Producing Wells

Depending upon the manner in which the well is completed, on pressure, and other physical characteristics of the well, inhibitors may be either pumped or dumped into the annular space between the tubing and casing of the well. Inhibitors are available in different solubilities, such as oil soluble, water insoluble; oil soluble, water dispersible; or, water soluble, oil insoluble or dispersible.

Solid stick inhibitors or pellets are available for treatment of "packed-off" wells. Similarly packed-off gas wells may be treated by the injection of large volumes of diluted inhibitor by pumping directly down the tubing allowing the solution to fall and coat the metal tubing.

The amount of inhibitor required varies from 1 quart for from 100 to 300 barrels of fluid produced. It usually costs an average of approximately $200 per year per well to treat.

For gas wells, the costs will vary from $0.25 to $1.50 per million cubic feet not including labor charges. In 1951 the NGAA estimated uninhibited corrosion costs to average $4.27 per MMCF. (6)

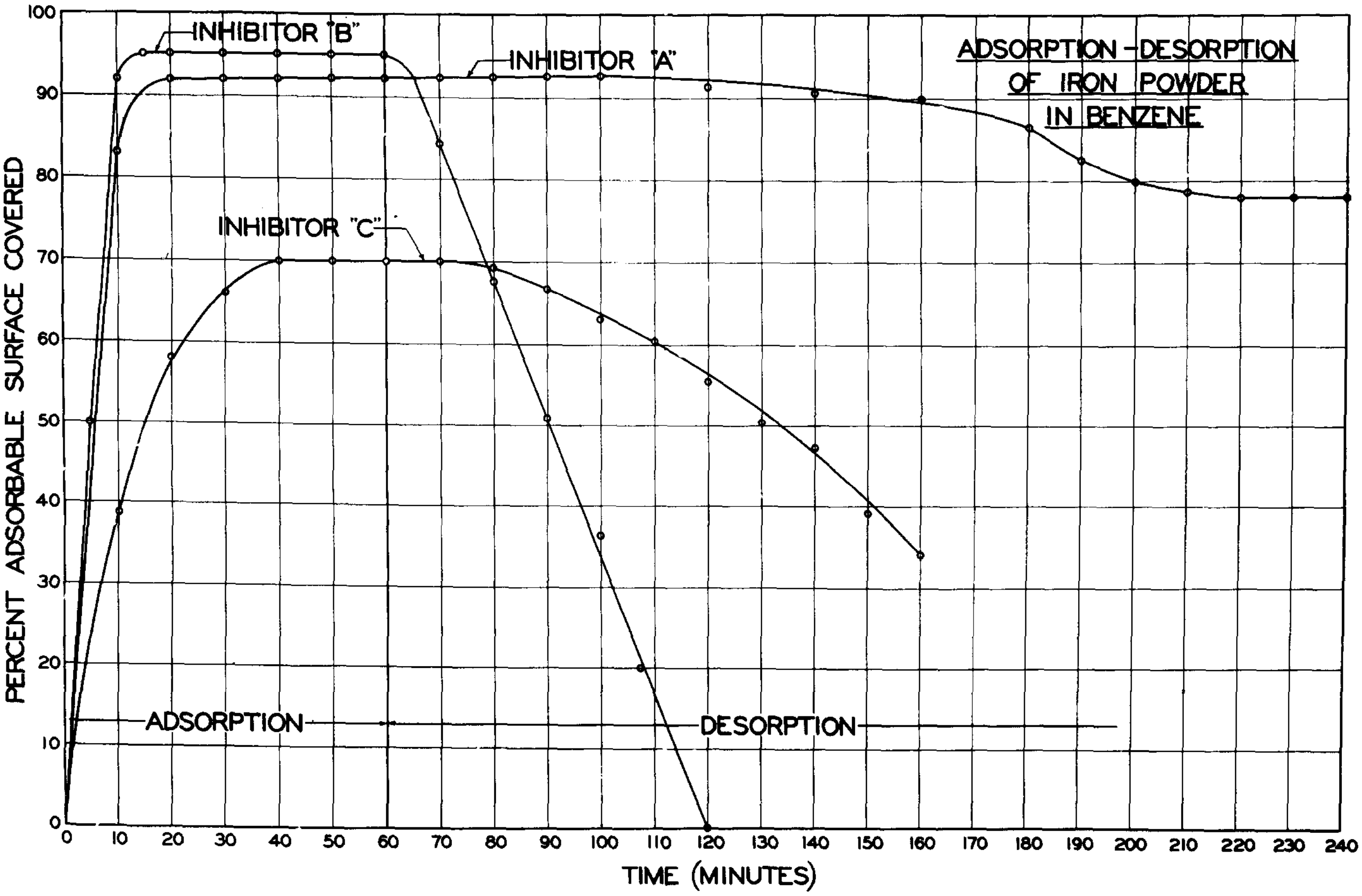


Figure 5

Refineries

All of the organic inhibitors presently used in refineries are of high enough moleclar weight that they will not distill up fractionating columns. Therefore, they are injected continuously into the overhead vapor lines ahead of condensers and exchangers where corrosion normally occurs. Many being oil soluble are returned with the reflux stream back into the column where corrosion mitigation is afforded to the top of the tower itself.

Usually from 6 ppm to 12 ppm are required for inhibition. The cost of treatment averages something in the order of from \$0.01 to \$0.03 per 1000 gallons of hydrocarbon. In addition to protection from corrosion, these inhibitors also tend to prevent fouling by salts and corrosion products by their oil-wetting effect.

Pipelines

Many pipeline companies have replaced inorganic inhibitors with their organic counterparts. Organics have the advantage of requiring only a single injection point. Many of the inorganics are difficult to handle or, being toxic, offer difficulty as a disposal problem. Many operators object to the addition of water even though the amount associated with the inorganics is small.

As was previously mentioned, Government specifications of many countries now require the use of organic oil soluble inhibitors. This has encouraged their usage where pipelines transport these products.

The cost of treatment varies from \$0.25 to \$1.50 per thousand barrels of product, except with Government fuels where the cost ranges from \$1.50 per 1000 barrels upward as the Government required larger concentration for subsequent protection to facilities such as tankers, aircraft carriers tankage, etc.

Other Uses:

Organic inhibitors are also being used in a variety of other applications. They are used in hydraulic oils in heavy hydraulic machinery for protection of machined parts. They are used in hydraulic brake fluids, in cooling water systems, in various anti-freeze formulations. Other uses include water flooding operations, in motor oil formulations and certain fuel oil additives must also possess corrosion inhibitive characteristics. Others find use in preventing corrosion in ballasted submarine fuel tanks handling diesel fuel. Light and heavy oil preservatives for storage of metal objects contain inhibitors.

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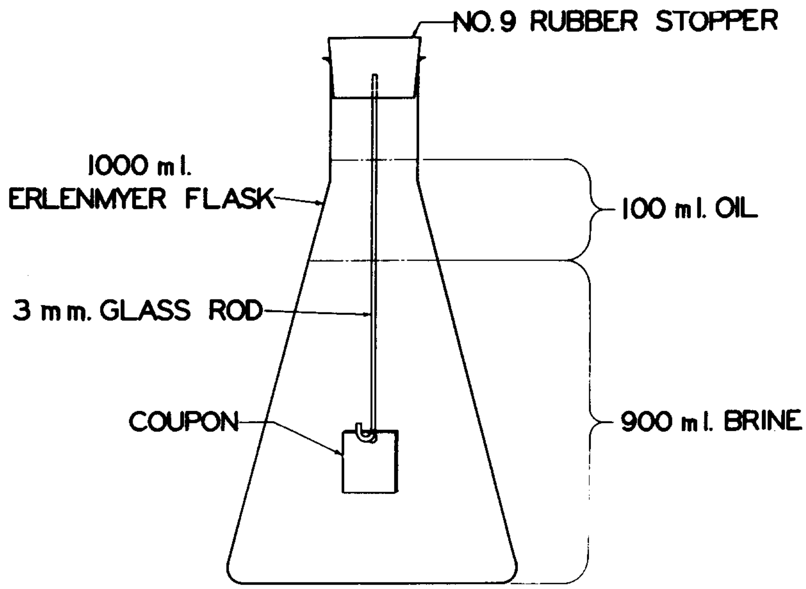
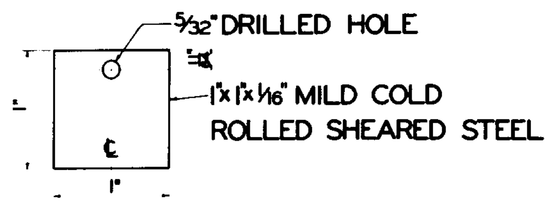


DRAWING A-TEST FLASK



DRAWING B-TEST COUPON

Figure 6