HYDROPHOBIC METAL LUBRICANT FILMS -NEW SOLUTIONS TO ENVIRONMENTAL PROBLEMS

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ABSTRACT

Hydrophobia, apart from the disease connotation, means fear of water. A Seldom mentioned fact of metallurgy is that there are "Hydrophobic" metals and alloys whose very nature is to resist wetting by water. As a corollary, these same surfaces agressively wet with oil and will maintain themselves oil wet in an oil/water flow stream by attracting oil out of the flow stream while repelling water. Since mineral scale deposition comes from the water component and not the oil, there will be a tendency for it to aggregate in the flow stream and and be swept out in the flow stream. Thus the system environment, being the oil/water mixture in the flow stream can be utilized to assist in solving scaling problems, particular at pressure drops and other scaling nodes. Examples will be presented wherein high energy ion deposited thin films of hydrophobic metals and alloys have been shown to resist scale formation while providing dry metal lubricity in a variety of actual installations.

In many cases, the formation of scale on a moving rod operating through an elastomeric seal will cause the seal to fail, resulting in the discharge of fugitive emissions to the environment. It has been demonstrated conclusively in many field applications involving stuffing box rubbers and lease motor valve stems that scale can either be prevented entirely or have its adhesion reduced to the point where an elastomeric seal will rub it off. The cost of such films is quite low and the economic benefits to the users in terms of increased service life alone make their use cost effective even without regard to the far more valuable consideration of reducing the incidence of and clean up costs associated with releasing fugitive emissions.

INTRODUCTION

The industry was first introduced to the benefits of thin film technology at the Fall Meeting of the Society of Petroleum Engineers in San Francisco in 1983. The paper, subsequently published in the JPT (1), dealt with the prevention of galling of high alloy thread connections. Baker Hughes has subsequently achieved worldwide success with the process which they offer under the trademark of "Bakertron". Among their many success stories has been the elimination of the need for pipe dope in the running of stainless steel pipe (2)(3).

The introduction of this technology initially met with a lot of resistance, primarily due to the fact that they function best at the micron thickness level. This thickness, less than half of a tenth of a mil, was first viewed as insufficient for anything, much less the rigors of oilfield applications. History has proven them to be very successful. High energy vacuum deposition technology is by no means new, The microelectronics industry as well as many innovations in modern, sophisticated weaponry depended upon such for existence.

This paper is not about thread galling. The effort actually started as an attempt to

answer an age old question being that of why a deteriorated or stuck elastomeric seal leaves such a hard and polish resistant mess in the sealbore from which it was removed. It would appear at first glance that decomposed rubber should be a loosely formed and easily removed residue. Anyone who has ever attempted the cleanup of a mandrel pocket can easily recall the difficulty of the job. The answer appears to be contained in the breakdown mechanism of polymers in general. Rubber is by nature a liquid and usually will return to the liquid state but for the crosslinking bonds provided by the rubber chemists. With age and environmental effects, these bonds will break down and, in the process, yield a reactive carbon that is free to attach itself to a metal in the sealbore forming a metal carbide. Thus a tightly bonded cutting tool will be inadvertently installed in the seal bore that, if not removed, will cut any new seals that are subsequently installed. This is a sobering thought when one considers the state of the sealing bore in a typical sidepocket mandrel in an offshore completion.

High energy film technology did appear to offer a solution by addressing the original rubber failure mechanism. The theory was that, if the deterioration of the seal was inevitable, there should be a way to limit and/or contain its destructiveness. By using a high energy vacuum deposition process to literally shoot the outer surface of the elastomer full of atoms of carbide forming metals creating a situation wherein the free carbons do not have to hunt far for a reactive metal and in fact, create a self improving structure by coating themselves with a thin outer layer of metal carbide. One further ingredient may be added to this stabilization of the elastomer. Since nickel carbide only occurs in the liquid and vapor state, it forms an excellent barrier to the migration of carbon and a nickel overcoat add further resistance to seal deterioration. One final consideration may now be easily addressed, being that of a hydrophobic metal lubricant outer coating to provide long term lubricity. This is inherent in the nature of dry lubricant metals and is enhanced when hydrophobic properties are accentuated for use in oil bearing flow streams.

The anticipated demand for these seals that seal hermetically while acting like elastomers was in all of the classic areas of seal application where the need for tighter seal compression was offset by the practical consideration of the destructive effect of friction increase at the rubber/metal interface. A prime illustration of this is the oil field field stuffing box. Here is a case where seals are tightened carefully at installation to avoid that amount of compression which will result in burning or outright siezing. These are in actual practice, more important considerations than that of the effectiveness of the seal. Thus, for years and years, this problem has been routinely, if not purposely, overlooked as a cause of unnecessary lease expenses and, more recently, as a controllable source of fugitive emissions.

As field testing proceeded, primarily in the Midway Sunset Field in California (figure 1), some very good results were obtained. It soon became apparent, however that another component of failure had to be addressed as the attention was turned to leaks from stem seals of motor valves. This had to do with another failure mechanism, being that of mineral scale deposits on the metal valve stem cutting the seals. It obviously would do little good to fix the surface of a seal if a file is then applied to remove it. It becomes necessary therefore to reduce the damaging effects of scale deposition. This may be either by eliminating it completely or by reducing its adhesion to the point where the contacting seal will wipe it off in normal stroking action. The first promising results were reported in the side by

side installations of Figures 2 & 3. It was not long before experimentors realized that a very promising and simplistic approach to general case scale control was suddenly appearing. Thus the transition of effort from seal performance to scale was a very natural one since they are natural co-conspirators in many failure modes.

FIELD TESTING PROGRAMS TO DATE

The unique ability of the Magion plating process to plate non-conductors with high energy ion bombardment has proven beneficial in several industries. Of particular interest has been that of allowing engineers to design higher installation compression into elastomeric seals for dynamic sealing applications. One such problem has been in aircraft hydraulic shafts where sufficient gland "squeeze" to totally stop leakage will be accompanied by an unacceptable amount of drag on the aircraft controls. The program of this paper began in the summer of 1991 when engineers from ARCO became interested in new approaches to the traditional (and usually ignored) problem of emissions from stuffing boxes. The problem has been the same for decades in that there is a point of installation compression beyond which the rubbers will sieze the polished rod and either burn or stop the motor. Therefore technique has always been to get as good a seal as possible without risking failure usually without regard to the actual effectiveness of the seal. The attendant odor that one encounters when driving through oil fields is caused in a large part by these emissions. With enforcement dates looming on the horizon for applicable sections of the clean air act, it would seem highly unlikely that over 600,000 of these highly visible installations in the United States alone are going to escape attention. The sole purpose of the effort reported herein was the search to find a new and simplifying technology to address this very old problem.

The repacking of stuffing boxes is an ongoing daily routine in every pumping field of any size. The decision was made to go directly to the field with the testing. This bypassing of the laboratory also bypasses the very real problem in achieving true dynamic similarity of so complex a system. Since the changeouts were ocurring frequently anyway there appeared to be no downside for the producer in taking this approach. It should be remembered that the sole purpose of the effort was emission control. This was considered sufficient gain from technology and the prospect of a service life increase was not even contemplated.

Initially, the experimentors were confronted with a seemingly hopeless number of variables. Some of these were; different types of rubbers, different manufacturers brand over a very wide cost range, different durometer hardnesses, impregnation flakes such as bronze or teflon for whatever reason and variations in well conditions both as to equipment and produced fluid. Many types of rubbers were rejected at the onset simply because they lacked the integrity to survive the high energy plasma conditions of the Magion deposition process. Others failed for a variety of reasons. Success began to be seen with the following operation.

On ARCO wells Maxwell 30 and 191 the typical mode of installation was $9\frac{1}{2}$ turns to handtight followed by another $\frac{1}{2}$ turn. The coated packing was installed to 12 rounds before the unit was started with a wrench required to go from 10 to 12 rounds. These wells pumped dry for 25 to 30 minutes before the well "pumped up" and at the first weeks inspection, no oil was observed spotting the polished rod. These rubbers subsequently lasted over 3 months where the norm was 10 to 14 days. Since this was in a steam flood, there was also opportunity to observe effects of temperature. The general conclusion is that the higher the temperature, the better will be the comparison with uncoated rubbers. Attention has, not unexpectedly, shifted from tighter sealing to increased service life. This is to be expected since on any given lease up to 40% of the pumpers time is spent in packing stuffing boxes. There are many variations in results ranging from nothing to 40 times life in some extreme cases. A popular number seems to be threefold in wells over 250 degrees to twofold in the more ordinary. No major producer would think of proceeding with a major field program such as drilling or massive fracturing without first doing a detailed present worth analysis. Although the managerial need are the same, there has probably never been such an analysis done on stuffing box rubbers as the present technology allows for. Stuffing box rubbers tend instead to be cast into the category of "rope, soap and dope" and true cost figures are almost impossible to obtain. Nevertheless, when such studies are done involving these coated rubbers, it does not require many months for present worth of savings to surpass a million dollars.

The big reason, of course, is improving sealing effectiveness in advance of mandantory requirements to do so. There are "Advance Compliance Credits" available for programs such as this that can dramatically increase its profitability. Here is an instance where improvements in emission source control actually come with a reduction in costs of operation.

In turning attention to another gross source of fugitive emissions, being that of leaks from the stem packings of motor valves, the first step was in coating the seals. Although showing some measure of success, the overiding failure mechanism was shown to be that of scale deposits on the stem surface that literally file their way throug the seal. Clearly something was necessary to ameliorate the destructive effect of the scale or no program could succeed. Toward that end there have been many Fisher motor valve stems Magion plated with hydrophobic metal lubricants placed in service throughout the country. Many have been reported well past the normal point of failure and still operating perfectly. The valves of Figures 2 & 3 were particularly encouraging since this test was in a steam environment with no oil in the flow stream. This is a worst case condition and it encouraged us to look further to other tools where scale buildup was an ongoing problem. Success is still being measured since the majority of these tools now in service have not failed.

The gas lift values of figure 4 were installed in wells near Farmington, N.M. where calcium carbonate plugging on a 90 day interval caused numerous interruptions for wire line work. Six of these values with hydrophobic metallurgy are still operating after almost a year in service. The circulation values of Figure 6 reflect a similar story in retarding barium sulfate in Prudhoe Bay Wells.

Perhaps the most detailed of results are those of Figures 6 & 7. This study is made possible by some very detailed instrumentation and offer good comparative insight. Note the smooth performance of the coated stem (actually the same stem in both cases) compared to the uncoated. Of perhaps more significance is the amount of load actually applied to sealing; 719 pounds compared to 0. Sealing is, of course, the valves prime function. There are other advantages that go beyond emission control. For example, in computer controlled multi-valve systems, erratic torquing can result in computer shut down of the entire system, whether it be a nuclear power plant or an offshore production platform or even a refinery. It is somewhat ironic that a utility company, whose only emissions are steam would be a leader in the study of this problem. If it is considered important to control-even steam emissions, then how much more so that of hydrocarbons and related sour gases.

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The methodology of surface treatments described herein are covered by United States Patents #4,420,386, 4,826,365 and 5,252,365. There are others pending.

CONCLUSIONS

It would appear that a sincere effort to achieve compliance with the laws regarding emissions has resulted in a surprisingly cost effective approach to lease operations. A promising approach to certain problems associated with mineral scale deposition has likewise been evolved. Those among the producers who are interested in pursuing any of this may find it somewhat difficult at first since most of the tool companies, fearing loss of after market in troubled times have expressed much reluctance to get involved. This is not at all unusual with new ideas and technology. The paper of reference 4 sums it up quite effectively and this word to the wise is quite a sufficient conclusion.



Figure 1 - Stuffing box rubbers that have been Magion plated with "White Gold'™ hydrophobic metal lubricant films for installation in the Midway Sunset steam flood fields of California.



Figure 2 - This gate valve as it appears after well over three years continuous service in a high temperature geothermal project. Prior to installation, the stem had been plated with a metal lubricant film that was found to have hydrophobic properties. Note the complete absence of leak residue from the stem seal.



Figure 3 - Valve similar to that of Figure 1 but of another brand and not plated with hydrophobic thin films. Installed at the same time and in parallel service with the valve of Figure 1, the residue from stem leakage is plainly visible in the area of the seal. This is actually the third seal assembly to be required in this valve since installation.



Figure 4 - Gas lift valve sub-parts that have been Magion plated with "White Gold"™ hydrophobic metal lubricant films prior to installation in salt water removal service. Results to date from several valves indicate an increase in service life prior to scale plugging of at least three times.



Figure 5 - Wire line retrievable chemical injector valve sub parts that have been Magion plated with "White Gold"™ hydrophobic metal lubricant films to prevent failure due to scale formation in oil wells in Prudhoe Bay, Alaska. Results to date show at least a threefold improvement. The chevrons were also plated to reduce seal sticking in the mandrel pocket.



Figure 6 - Dynamic analysis of the stroking action of a Fisher Motor Valve. Test performed at the Camanche Peak Nuclear Power Plant of TU Electric.



Figure 7 - Repeat of Figure 6 test except with valve stem and packing Magion plated with "White Gold"™ Hydrophobic Metal Lubricant films. Test performaed at the Camanche Peak Nuclear Power Plant of TU Electric.

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