THE IMPACT OF ROLLING OIL LUBRICITY AND NEW SYNTHETIC LUBRICANT TECHNOLOGY ON CLEAN STEEL PRODUCTION[1]

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Abstract

Previous work by the author has indicated a direct correlation between rolling oil lubricity and the production of clean surface “full-hard” rolled sheet product and annealed sheet product. This relationship is borne out by the existence of a primary layer of organometallic residues strongly adhering to the steel strip surface even after other surface oils and iron particulates have been removed by solvents such as hexane. We have named this surface residue layer “embedded residue”, and it is comprised of metallic soaps (primarily iron soaps, of course) in a matrix of “ground-in” iron fines, fatty acids and other rolling oil components. This residue is easily measured in the field or the laboratory and is directly related to the lubricity found in the roll bite. Lower roll-bite lubricity results in correspondingly higher “embedded residues”, with a concomitant increase in Leco surface carbons for the annealed sheet. These residues, whether full-hard or from the anneal interfere with subsequent processing of the sheet. As such, a study was undertaken to observe the effect of higher lubricity synthetic esters on the formation of this layer. The hypothesis is that since the embedded residue layer is so strongly correlated with roll-bite lubricity, then an increase in roll-bite lubricity should naturally decrease the volume of this “embedded residue” layer. Since previous studies had all involved the more obvious measures to increase rolling lubricity such as increasing rolling oil saponification number, reducing roll-roughness, or increasing oil volume on the sheet (“plate-out”), this study would examine the potential of increasing the lubricity beyond that which was considered the “ultimate” in lubricity: a “fully-fatted” or 100% C-18 fatty acid chain length synthetic lubricant. As such, a series of higher chain length synthetic esters, C-20 and above, have been examined. The initial laboratory work and field experience with these esters does verify higher lubricity in the rolling oil than has been previously available. This has translated into lower embedded residues, as well as other benefits resulting from this increase in lubricity. The following data will describe the methods used to test these hypotheses, and the results that were found.

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EXPERIMENTAL

The various residues on full hard sheet samples were measured and characterized by the following techniques, depending on whether they were laboratory or field measurements:

For the determination of full hard sheet residues, samples were taken from the tail of the coil, on-gage, approximately 15-20 meters into the coil. It should be noted that samples have also been taken from cleaning lines and rewind lines wherein samples could be selected from anywhere within the coil. The measurement techniques remain the same in each case, but the results will differ. Therefore, it is important to sample from the same position on the coil for every measurement.

The steel samples are measured for total surface area (top and bottom), weighed to the nearest 0.1mg., and are then rinsed with hexane solvent for two times on each side (approximately 10-15 seconds; the time is not so important as that the entire sample is completely rinsed). No rubbing, wiping, or mechanical soil removal of the sample takes place during the hexane wash. The recommended surface area to be tested is from 200-400 sq.cm. The hexane rinse from the sample is then collected in a beaker and saved for further analysis. Meanwhile the hexane samples are re-weighed to 0.1 mg. and are allowed to dry in ambient air for 5 minutes. They are then wiped with either filter paper or white paper towels until no additional residue is apparent on the paper upon wiping the sample. This sample is allowed to set for another 5 minutes and then re-weighed again to the nearest 0.1 mg. The first weight differential between as received and hexane washed is considered to be the “total solvent extractable residue”, and the second weight differential from paper wiping is considered the “total embedded residue”. These two measurements are the typical residue measurements performed in the field, or for when a quick, yet reliable, indication of residues is required. The measurements are reported as mg./sq. meter.

For a more detailed analysis of the total solvent extractable residue, the hexane rinsings that were collected in the beaker are warm filtered (approx. 35 C) through coarse filter paper, the solvent evaporated from the filtrate, and the resultant oil weight measured. This is subtracted from the “total solvent extractable residue” to give a comparison of oil and particulate in the total residue sample (the assumption is made that the vast majority of particulate is iron particles). If an even more definitive measurement of iron particles is required, then the filter media may be digested with HCl and the iron content determined by ICP or AA.

For a more comprehensive analysis of the “total embedded residue” samples, the filter paper or paper towels used to wipe the samples can be digested with HCl as above and the iron content determined. We have also analyzed the hexane washed sample numerous times for FTIR reflectance spectra. Obviously this must be done prior to wiping the samples. This reflectance FTIR technique indicates strong absorbance’s in the ester, fatty acid, and metal soap region, as well as weaker absorbance’s for various rolling oil additives.

Typical residues for full-hard sheet meeting automotive quality standards are as follows:

Oil	50-250 mg./meter
Iron Particulate	20-50 mg./meter
Embedded Residue	50-150 mg./meter

The surface carbon levels on annealed sheet were determined by LECO carbon analysis. This was done by using the temperature programmable LECO RC-412 carbon analyzer. The temperature ranges measured are from 400-500 C (designated as phase 1 and 2 carbons), and from 500-670C (designated as phase 3 carbons). The results are given in mg. of carbon per sq. meter. The length of time to transition through these 3 phases (or temperature gradient) is about 10 minutes. Typical phase 3 LECO carbon values for full-hard sheet meeting automotive quality standards are: 0.2-1.5 mg./meter.

The rolling oil ester evaluation was accomplished by using a single stand reversing mill, instrumented for roll force, motor load, tension, incoming and exit gage, and speed. A series of synthetic trimethylolpropane esters of fatty acid chain length from C-12 to C-22 were evaluated as well as traditional glycerol based natural esters such as animal fat of fatty acid chain length C-18 and C-16. The results were evaluated as the percent reduction obtained at near limiting roll force. The various candidate oils were evaluated as 5% emulsions in water using a moderately dispersive emulsion of relatively high plate-out so that the plate-out or emulsion characteristics of the oil were not the limiting factors. The solution temperature was 60 C.

To correlate these results with a bench-top instrument the EHL (elastohydrodynamic) test device was selected. This device has demonstrated perfect correlation with the rolling mill results as opposed to more traditional bench-top devices such as the falex and 4-ball test rigs. The test parameters were slide to roll ratio and speed. The results were expressed as a function of traction coefficient (coefficient of friction). This was analogous to the roll force versus percent reduction curve found for the rolling mill tests. Therefore, reduced coefficients of friction at high slide to roll ratios were desirable. The data collected for both the rolling mill and the EHL device were compared for correlation and found to be in agreement.

DISCUSSION

Our work with sheet surface residue analysis for the past 17 years indicates that the critical residue layer for producing clean sheet, both full-hard and from the anneal, is the “total embedded residue layer”. In addition, this layer is directly affected by the lubricity found in the roll bite during rolling. Let us examine these two factors separately.

For years it was recognized that iron on the sheet and in the solution seemed to correlate in some fashion with the ultimate cleanliness of the sheet surface from the anneal as well as directly from the mill. However, there seemed to be many exceptions to this, as low solution irons did not always give clean sheet, and high solution irons often provided very clean sheet. Further, the amount of iron found in a simple “weigh – strip – weigh” solvent wash did not always correlate with clean steel either. Clearly something was missing, and at the same time it became apparent that there was a residue left on the sheet after solvent washing that was not being measured. This, of course, turned out to be the embedded residue layer. At first this was thought to just consist of iron, but it was noticed that the embedded residue layer for full-hard samples was always higher than the embedded residue layer for annealed samples. Clearly something was burning off in the anneal from this residue layer. Reflectance FTIR of this layer demonstrated that the organic phase of this layer was composed primarily of iron soaps and some rolling oil. This formed a tenacious, sticky, low-volatility residue that acted as a “binder” for “ground-in” iron fines formed in the roll bite. The percentage of iron of the total weight in this layer varied generally from about 30-70%.

By testing various hypotheses over a long period of time (many years), it was found that the embedded residue was directly correlated with lubricity in the roll-bite. This roll-bite lubricity could be affected by many factors such as rolling oil lubricity e.g. saponification number, roll roughness, tramp oil, percent reduction in the stand, oil volume (plate-out), steel hardness (grade), etc. However, in every case, anything that decreased the lubricity in the roll-bite, whatever the source, always increased the quantity of embedded residue. So the relationship was clear, an increase in lubricity in the roll bite decreased embedded residues, a decrease in lubricity conversely increased the embedded residue.

This effect was then correlated with LECO carbon analysis for annealed steel samples for which the embedded and total residues were known. For this study a temperature programmable LECO carbon analyzer was employed. It was soon found that as the LECO oven temperature was increased that there two zones where carbon evolution peaked. These were the zone from 400-500 C and the zone from 500-670 C. The first zone was eventually further resolved to find that there were two phases in this first zone as well. The relationship of the carbon evolution in these 3 phases, then, was found to correspond primarily to the following: The total solvent extractable residue and any oil residual from handling the sheet after the anneal e.g. rust preventive oils or fingerprints, primarily impacts phase 1 and 2, whereas, the embedded residue primarily impacts phase 3, particularly in the region of 630-650 C.

This was significant also, as the evidence in the field was that the carbon found in phase 1 and 2 was primarily related to “loose smut” on coils, whereas the carbon found in phase 3 was highly correlated to the graphitic type of carbon issues such as poor plating, galvanized, poor cleaning at cleaning lines, and poor paintability. Clearly, although neither residue was desired, the carbon residue from phase 3 was the most detrimental to product quality. In fact, carbon numbers in the phase 3 zone higher than 5.0 mg. sq./meter were determined to have an exceptionally high level of plating failures. A number less than 2.0 mg./sq.meter was found to be desirable, with the lower the number the better.

Since we knew that the embedded residue layer was primarily responsible for the phase 3 carbon levels, we knew that to control this layer would result in desirable clean sheet quality. However, we also knew that the embedded residue layer was directly related to lubricity in the roll bite, so it was paramount to improve the lubricity in the roll bite if we were to reduce the embedded residue layer, and therefore also the phase 3 carbons, which would result, of course, in cleaner sheet.

So the task was clear, increase the lubricity as much as possible in the roll bite, consistent with mill practices and capabilities. Also, it was clear that for higher saponification rolling oils, an appreciable amount of higher-volatility sulfur additives (“synthetic sulfur”) would be required to avoid the side-effect of smut on the coils from the less volatile esters. This was accomplished by using sulfur additive contents from 1.8-2.5% generated from a sulfur additive of considerably higher volatility than the traditional sulfurized esters.

The next step in this ongoing evolution of improved sheet cleanliness performance was to evaluate synthetic esters of various lubricities compared to the traditional animal fats and conventional synthetic esters. Traditional bench-top lubricity test devices such as the falex and 4-ball test rigs have notoriously poor correlation with rolling oil lubricity. Therefore, it was felt that the only reliable test was to use a small rolling mill to evaluate the lubricants. This was done using standardized emulsions of the rolling lubricants, and it soon became clear that the lubricity of the higher chain length fatty acid synthetic lubricants far exceeded that of the shorter chain synthetics and they also out-performed the traditional fatty based esters. Of particular interest were the C-20 and C-22 synthetic esters.

It was clear, however, that the use of the rolling mill for various test variables was not feasible long-term because of cost and time constraints. Therefore, the use of the elastohydrodynamic test device (EHL device) was examined to see how it compared with the rolling mill. In every case, the EHL results paralled those of the rolling mill, and were also able to predict rolling mill performance for lubricity in an accurate manner.

Therefore, the EHL test device can now be used to screen new synthetic esters as well as completely formulated products for rolling lubricity. This, of course, also correlates directly with the embedded residue results and ultimately with the carbon numbers for annealed sheet and the perceived and actual sheet cleanliness. In other word, increasing the roll-bite lubricity through the higher chain length synthetic esters will decrease embedded residues and result in lower phase 3 carbons. These effects will provide steel easier to plate and to clean, as well as, by definition, easier to roll.

CONCLUSION

We have found that the use of simple full-hard and annealed sheet residue analysis can be predictive for sheet steel surface cleanliness. In addition, it can be diagnostic in that it can direct the mill and rolling oil personnel as to how to improve their processes. The reason for this is that the surface residues are directly correlated with lubricity in the roll-bite as well as other rolling solution parameters. Further, they are also directly correlated with the formation of surface carbon that may be characterized in identifiable temperature zones in the LECO carbon analyzer. The carbon numbers found in these zones (phases) is also directly correlated with sheet steel cleanliness and quality as shipped to the customer.

The most effective approach therefore, has been to use the highest lubricity oil possible consistent with the mill’s operating conditions. In addition, the use of higher levels of high-volatility sulfur additives is advisable.

Finally, for those mills that are using conventional fatty oils or synthetic oils of traditional fatty acid chain length, recent rolling mill evaluation indicates that the use of higher lubricity synthetic esters is likely to improve sheet cleanliness as well as rolling performance. The EHL lubricity bench test device can screen these new synthetics, and suggest optimum rolling oil lubricity. Initial field results with these new synthetics indicates cleaner sheet surfaces and increased rolling lubricity.