Chapter 7

General Conclusions, Recommendations and Future Work

In this work, the relationship between cold rolling oil formulation composition, the formation of thermally-stable oil decomposition deposits and the effect of such deposits on 55Al-43.4Zn-1.6Si hot dip metallic coating quality has been investigated. Both fully-formulated commercial cold rolling oils and several key cold rolling oil ingredients have been studied and the impact of processing parameters such as cleaning furnace atmosphere and substrate composition has been assessed. This Chapter summarises the main conclusions drawn from this research and offers recommendations and suggestions for future work where appropriate.

Three common classes of cold rolling oil ingredients which decompose to leave high levels of thermally-stable residue have been identified as follows: base esters, sulfurised extreme pressure (EP) lubrication additives and phosphorus-based anti-wear (AW) additives. The thermo-oxidative and thermo-reductive decomposition properties of a variety of ingredients within each of these three classes have been studied by Thermogravimetric Analysis (TGA) and Pressure Differential Scanning Calorimetry (PDSC) techniques. Infrared spectroscopy has also been used to characterise chemical changes occurring during additive thermo-oxidative decomposition. The influence of variations in additive chemical structure on the residue-forming tendency of both the neat additives and, for the sulfur and phosphorus additives, blends of the additives at different concentrations in a commercial cold rolling base ester have been evaluated by a derivative of the PDSC 2-peak test developed by Zhang and co-workers.[1, 2] Finally, the impact of additive thermal decomposition residues on 55Al-43.4Zn-1.6Si hot dip metallic coating quality has been assessed by performing industrial hot dipping trials and experimental hot dipping simulations and characterising the resultant coatings visually and by optical microscopy and Scanning Electron Microscopy (SEM) techniques.

The results obtained reveal that the formation of thermally-stable decomposition deposits can be minimised by tailoring base ester chemical structure. Esters containing highly unsaturated alkyl chains and hydroxyl functional groups decompose to form greater levels of carboxylate and oxy-polymeric residues due to the occurrence of oxidation, crosslinking and condensation polymerisation reactions. These residues adversely affect hot dip metallic coating quality by causing the formation of uncoated defects. The amount of residue formed by base ester decomposition can be minimised through the use of a thermo-reductive HNX atmosphere and by reducing the level of alkyl chain unsaturation.

Sulfurised lubrication additives have the most severe detrimental impact upon 55Al-43.4Zn-1.6Si coating quality; they cause the formation of gross uncoated defects at even low (≥ 1.0 % w/w sulfur) concentrations in additive/base ester blends. However, sulfurised additive chemical structure has a considerable influence on both uncoated defect severity and the level and chemical nature of thermally-stable residues formed. Sulfurised hydrocarbons decompose to form low levels of sulfur-/sulfur oxide-based residues which contain very little hydrocarbon content and have a negligible effect on metallic coating quality even at high (2.5 % w/w) sulfur concentration. In contrast, sulfurised triglycerides decompose to form significant amounts (up to 11 % by mass) of carboxylate- and radical-recombination product-based residues and have a considerably more severe impact upon metallic coating quality.

Although phosphorus-based lubrication additives also decompose to form high levels of residue (up to 13 % by mass) comprising of amorphous short-chain polyphosphates, this residue has no noticeable impact upon metallic coating quality, even when the additives are incorporated at very high (2.5 % w/w phosphorus) concentration in additive/base ester blends.

Given these findings, the following recommendations can be made:

- commercial cold rolling oils should be formulated using saturated, as opposed to highly unsaturated, base esters to minimise the formation of thermally-stable high molecular weight material during the furnace cleaning process;
- in oil formulations where EP lubrication additives are required, sulfurised hydrocarbons should be used instead sulfurised triglycerides;
- wherever possible, phosphorus-based EP/AW additives should be incorporated into cold rolling formulations in place of sulfurised additives due to their mimimal impact upon hot dip metallic coating quality.

Although these recommendations are all subject to factors such as maintaining appropriate emulsification and lubrication properties, the opportunity exists for research to be conducted into developing new sulfur-/phosphorus-based EP/AW additives which are tailored to improve lubrication performance whilst maintaining acceptable hot dip metallic coating quality. Furthermore, by studying more complex additive/base ester blends (incorporating multiple, as opposed to single, additives) synergistic effects on oil residue-forming tendency and impact upon hot dip metallic coating quality can be investigated. In particular, research into the effect of anti-oxidants on the additive/base ester decomposition process is required to investigate strategies for minimising the formation of high molecular weight material (and hence, thermally-stable residues). Improvements can also be made in the experimental hot dipping procedure used to evaluate additive impact upon 55Al-43.4Zn-1.6Si coating quality. Research could be done to develop a method for either partially oxidising the additive/oil film *in situ* in the hot dipping apparatus, or pre-oxidising the additive/oil blend in bulk before it is applied to the steel test sample. In addition, investigating how the experimental error associated with determining the % uncoated defect area can be reduced would assist in distinguishing between the effects of different additive/ester blends on metallic coating quality.

The effect of two key process parameters, substrate (catalyst) composition and furnace atmosphere composition, on the thermal decomposition and residue formation properties of a fully-formulated cold rolling oil have also been assessed by conventional and modulated (MTGA) thermogravimetric analysis techniques. The activation energy associated with oil decomposition events has been calculated and the process of oil removal from a steel substrate has been visualised by high temperature Laser Scanning Confocal Microscopy (LSCM).

The conventional TGA results obtained by analysing the rolling oil thermo-oxidative decomposition behaviour in the presence of aluminium, steel and 50 % w/w iron oxide powder catalysts confirm that an aluminium substrate can be validly used to mimic rolling oil removal from cold rolled steel. However, the presence of iron in the catalytic material shifts the oil volatilisation processes to lower temperature, an effect which is compounded by increasing the iron to oil ratio. The level of oily residue remaining at 500 ^{o}C is increased by the use of a steel substrate, an observation which can be attributed to oil reactions with the substrate surface to form metal salts. The activation energies measured confirm the superior activity of steel in catalysing oil oxidation. However, the increase in activation energy observed with increasing conversion using both steel and aluminium substrates evidences that the residues formed become more thermally stable as the oil decomposition process advances. LSCM analysis of the oil removal process from cold rolled steel confirms the identity of oil thermo-oxidative decomposition reactions but also suggests that substrate oxidation may play a significant role in the residue formation process; the formation of isolated areas of surface oxides could nucleate the aggregation of oily residues and potentially account for the observance of uncoated defects in hot dip metallic coatings.

The results obtained by studying the rolling oil removal process from a steel susbtrate under several different gas atmospheres (oxygen, nitrogen, argon and 5 % hydrogen-95 % nitrogen, or HNX) show that a reducing HNX atmosphere is the optimal gas environment for effective oil removal as a greater amount of oil mass is lost at lower temperatures and less thermally stable products are formed. This increased oil removal efficiency corresponds to higher activation energy as measured by the MTGA and Flynn-Wall-Ozawa[3-5] techniques. A highly oxidising atmosphere has detrimental effects on the oil removal process as it causes the formation of thermally stable products and high amounts of residue within the maximum temperature range employed in the industrial furnace cleaning process.

The recommendations which can be made from this research include:

- the atmosphere within the continuous annealing furnace should be tailored to contain as little oxygen/ carbon oxides as possible, and
- batch annealing may be more appropriate process to use where steel is to be hot dip coated as HNX minimises oil residue formation.

Future work in this area could include investigating the phenomenon of rolling oil aggregation at sites of oxidation on the steel surface and whether the aggregates correspond to areas where uncoated defects are formed in hot dip metallic coatings. Furthermore, studies could be undertaken to more closely simulate the conditions present in the continuous annealing furnace (gas composition, dew point, heating rate) and their effect on rolling oil decomposition and residue formation.

A predictive test for screening cold rolling oils with respect to their impact upon hot dip metallic coating quality has been developed by studying the thermal decomposition properties of twelve different commercial cold rolling oils by PDSC and TGA and relating these properties to hot dip metallic coating quality results. PDSC and TGA parameters indicative of oil residue formation characteristics have been used to calculate three indices (a PDSC parameter index (PI), a TGA parameter index (TI) and a combined parameter index (CI)) for gauging oil impact upon metallic coating quality. Whilst the CI and TI indices were incapable of ranking oil performance with respect to metallic coating quality due to their dependence on oil volatilisation properties as opposed to residue formation and the closeness of the TGA parameters values, the PI index accurately predicted oil impact upon metallic coating quality; the sequence of the oils determined by the PI index corresponded to the oil sequence with respect to the metallic coating quality results.

There are many areas in which the predictive test developed within this research can be improved. By undertaking experimental hot dipping simulations, the % uncoated defect area for each rolling oil formulation could be determined and correlated to the PI index to provide a more quantitative test for screening new oils. In addition, the inclusion of 'reference' oil formulations (three oils which produce a defect free coating, pinhole uncoated and gross uncoated defects respectively) into the test procedure would facilitate the interpretation of results for unknown rolling oil formulations by allowing ranges over which the PI index indicates that an oil will produce gross, pinhole, or defect free metallic coatings to be determined. Lastly, further development of TGA test conditions could improve the ability of TGA to distinguish between the different oil formulations so that it could be incorporated into a comprehensive index.

References

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