Chapter 6

Development of a Thermal Analysis Test for Predicting Rolling Oil Performance With Respect to Metallic Coating Quality

6.1 Introduction

In the coated steel products industry, metallic coating integrity is of utmost importance to both product performance and downstream processability. The purpose of the metallic coating is to provide barrier and galvanic protection to the steel substrate[1] and the occurrence of defects within the coating can lead to poor product durability, inferior aesthetic appearance[2] and time delays in the application of subsequent coatings such as paint. 55Al-43.4Zn-1.6Si (Zincalume®) coated steel products are increasingly being used within the building and manufacturing industries in place of traditional galvanised products.[3] One of the most prevalent types of defects that can occur within 55Al-43.4Zn-1.6Si coatings is uncoated defects (figure 6.1).[4]

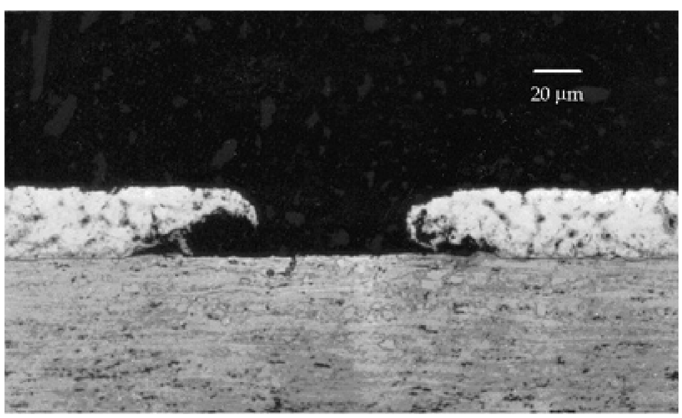

Figure 6.1 SEM image of an uncoated defect, courtesy of BlueScope Steel®.

Uncoated defects are discontinuities, or bare spots, in the hot dip metallic coating structure. Many factors have been associated with the occurrence of uncoated defects, including incomplete pickling of the steel substrate, insufficient reduction of oxides on the strip surface and the condensation and oxidation of zinc on the steel surface.[2, 4-12] However, residues remaining after the cold rolling and the direct fired furnace processes have often been cited in the literature as being problematic to downstream processing and further surface treatment.[2, 4, 9, 10, 13-18]

The process via which oily residues give rise to the occurrence of uncoated defects involves the inhibition or prevention of intermetallic alloy layer growth.[2] It is suspected that changes to steel surface chemistry due to the persistence of oily residues after cold rolling and furnace treatment alter the steel surface energy and preclude the alloy/steel reaction which is essential for intermetallic layer formation and 'wetting' of the steel surface by the molten alloy.[5] The impact of rolling oil formulations upon metallic coating quality is currently evaluated by performing industrial hot dip coating trials. These trials are both time-consuming and costly so that the development of a rapid, laboratory-based screening method is required to facilitate the formulation of improved rolling oils.

Thermal analysis techniques such as Thermogravimetric Analysis (TGA) and Pressure Differential Scanning Calorimetry (PDSC) commonly form the basis of predictive tests used to evaluate oil oxidative stability[19-27] and residue-forming properties.[28, 29] Parameters measured using these techniques, including the TGA onset temperature of mass loss and the PDSC Oxidation Induction Time (OIT), peak maximum temperature and peak enthalpy, have been successfully correlated with the results of traditional oil oxidation and deposit-formation tests to enable the screening of oils with respect to their performance across a range of automotive, food and metal-working applications. The use of PDSC and TGA techniques to study the properties of commercial cold rolling oil formulations is considerably less extensive[13] and rolling oil residue formation is typically evaluated using wet chemical, infrared and mass spectrometric techniques.[14, 30-34] The possibility of developing a predictive test based on PDSC and/or TGA to screen rolling oil formulations with respect to their likely impact on metallic coating quality has never been investigated.

In this study, the effect of twelve commercial cold rolling oil formulations on 55Al-43.4Zn-1.6Si coating quality has been evaluated by performing industrial hot dipping trials and classifying the oils according to the level of uncoated defects they produce. Comparison between the coating results and the residue-forming characteristics of the oils according to several TGA and PDSC test parameters has enabled relationships between oil composition, residue formation and uncoated defect severity to be assessed. The parameters have also been used to develop a new method for screening oils with respect to their likely impact upon 55Al-43.4Zn-1.6Si coating quality.

6.2 Experimental

6.2.1 <u>Sample Preparation</u>

6.2.1.1 Materials

The properties of the materials used are described in Chapter 2.2 as follows:

- fully-formulated, commercial cold rolling oils – section 2.3.1.1 and table 2.1;
- cold rolled steel - table 2.3;
- 55Al-43.4Zn-1.6Si alloy - table 2.4;
- shellite solvent - section 2.2.5;
- oxygen gas - section 2.2.6, and
- TGA and PDSC consumables - section 2.2.7.

6.2.1.2 Preparation of 55Al-43.4Zn-1.6Si Coated Steel Samples

55Al-43.4Zn-1.6Si hot dip metal-coated samples were prepared according to the industrial hot dipping trial procedure described in Chapter 2 (refer to section 2.3.4).

6.2.2 <u>Characterisation of Thermal Decomposition Behaviour</u>

6.2.2.1 TGA

TGA analysis of the rolling oil formulations was carried out under oxygen according to the conditions and procedure described in Chapter 2 (refer to section 2.4.1).

6.2.2.2 PDSC

PDSC analysis of the rolling oil formulations was carried out according to the conditions and procedure described in Chapter 2 (refer to section 2.4.2).

6.2.3 <u>Data Evaluation</u>

6.2.3.1 TGA and PDSC Results

Four key parameters were selected to assess the likely impact of the oil formulations on 55Al-43.4Zn-1.6Si hot dip metallic coating quality:

- % residue at 500 ^oC (500 ^oC is the average maximum temperature employed during the industrial continuous annealing process, whereby the steel surface is cleaned of rolling oil residue) determined by TGA;
- % B/A ratio determined by both TGA and PDSC according to the method outlined for triglycerides in Chapter 3.2;
- secondary region maximum rate of mass loss/heat flow temperature (T_{max} in the temperature range 300-500 ^oC) determined by both TGA and PDSC, and
- decomposition end temperature (T_{end}; the temperature at which no further mass loss/heat flow events are observed) determined by both TGA and PDSC.

These parameters are associated with the residue-forming characteristics of an oil, which in turn are related to the occurrence of uncoated defects.

6.2.3.2 Metallic Coating Quality Results

Qualitative analysis of the impact of the twelve rolling oil formulations on 55Al43.4Zn1.6Si hot dip metallic coating quality was performed by visually inspecting the metal coated samples (refer to section 2.4.5.1 in Chapter 2). Based upon this inspection, the samples were classified as possessing defect-free coatings (no visible uncoated defects), medium to pinhole uncoated (defects in the micrometre to millimetre size range) or gross uncoated defects (millimetres to centimetres in dimension).

6.2.4 Raw Data Summary

The metallic coating quality data and average TGA and PDSC parameter values determined for each of the oil formulations are given in table 6.1. The oils are coded according to whether they produce defect-free (light grey), medium to pinhole uncoated (mid grey) or gross uncoated (dark grey) defects.

6.3 Results and Discussion

6.3.1 Rolling Oil Impact on Metallic Coating Quality

The impact of the twelve rolling oil formulations on 55Al43.4Zn-1.6Si coating quality was evaluated by performing industrial hot dipping trials. Visual inspection of the resultant coated samples indicates that seven of the twelve commercial old rolling oil formulations (BSLWP1.1, 560453, 560350noS, CAT29, SB4198, U1388501 and XR81627) produce defect-free coatings, four formulations (560350, N609DPD, XR82154, XR81628) cause medium to pinhole-uncoated defects and one formulation (XR81629) causes gross uncoated defects. Figure 6.2 shows images of typical defect-free (A), medium to pinhole uncoated (B) and gross uncoated (C) samples produced using oils 560453, 560350 and XR81629 respectively.

The defect-free coating produced using oil 560453 (figure 6.2A) displays normal-sized spangles (0.2-5 mm diameter),[2] no uncoated areas and is representative of the coatings produced using oils 560350noS, BSLWP1.1, CAT29, SB4198, U1388501 and XR81627. The uncoated defects observed for the 560350-treated sample (figure 6.2B) are base-uncoated in nature,[4, 5, 9, 10] generally elliptical in shape and are grouped together in clusters of ~ 20 at several locations across the sample surface. They range in size from millimetres down to tens of micrometres in diameter, constituting medium to pinhole uncoated.[5] The uncoated defects present in the N609DPD, XR82154 and XR81628-treated samples are of similar size, shape and spatial distribution. The coating produced using oil XR81629 (figure 6.2C) displays gross base-uncoated defects[5] and although the majority of these defects are elliptical in shape, some larger uncoated areas appear as streaks in figure 6.2C.

Table 6.1 Summary of metallic coating quality, TGA and PDSC data obtained for the twelve rolling oil formulations. Values given are the average of three individual runs and errors are less than ± 10 % for all measurements except the % residue at 500 °C (error = ± 20 %).

= defect-free   = medium / pinhole-uncoated   = gross-uncoated

Oil Formulation	Metallic Coating Quality	PDSC			TGA			
		T_{max} (°C)	% B/A ratio	T_{end} (°C)	T_{max} (°C)	% B/A ratio	T_{end} (°C)	% Residue at 500 °C
XR81627	Pass	380.3	4.22	483.8	470.3	18.0	514.8	1.56
BSLWP1.1	Pass	418.0	23.8	478.4	479.1	33.1	517.5	1.53
560453	Pass	414.9	18.3	486.3	476.5	39.7	523.6	2.70
560350noS	Pass	421.6	18.5	479.4	477.5	34.0	514.2	1.30
U1388501	Pass	410.2	23.1	491.7	478.1	41.5	524.9	3.20
SB4198	Pass	387.2	4.39	492.2	480.5	33.8	523.8	3.30
CAT29	Pass	415.9	18.2	499.6	478.9	35.3	510.5	3.45
N609DPD	Medium to Pinhole	414.7	27.3	494.0	476.9	37.4	541.1	1.20
560350	Medium to Pinhole	420.3	30.6	493.7	477.7	36.4	508.8	1.46
XR82154	Medium to Pinhole	407.6	32.7	499.8	476.4	46.7	519.5	3.80
XR81628	Medium to Pinhole	416.4	21.0	498.5	475.1	37.8	522.4	3.60
XR81629	Gross	416.6	30.3	498.7	475.9	45.6	518.0	3.46

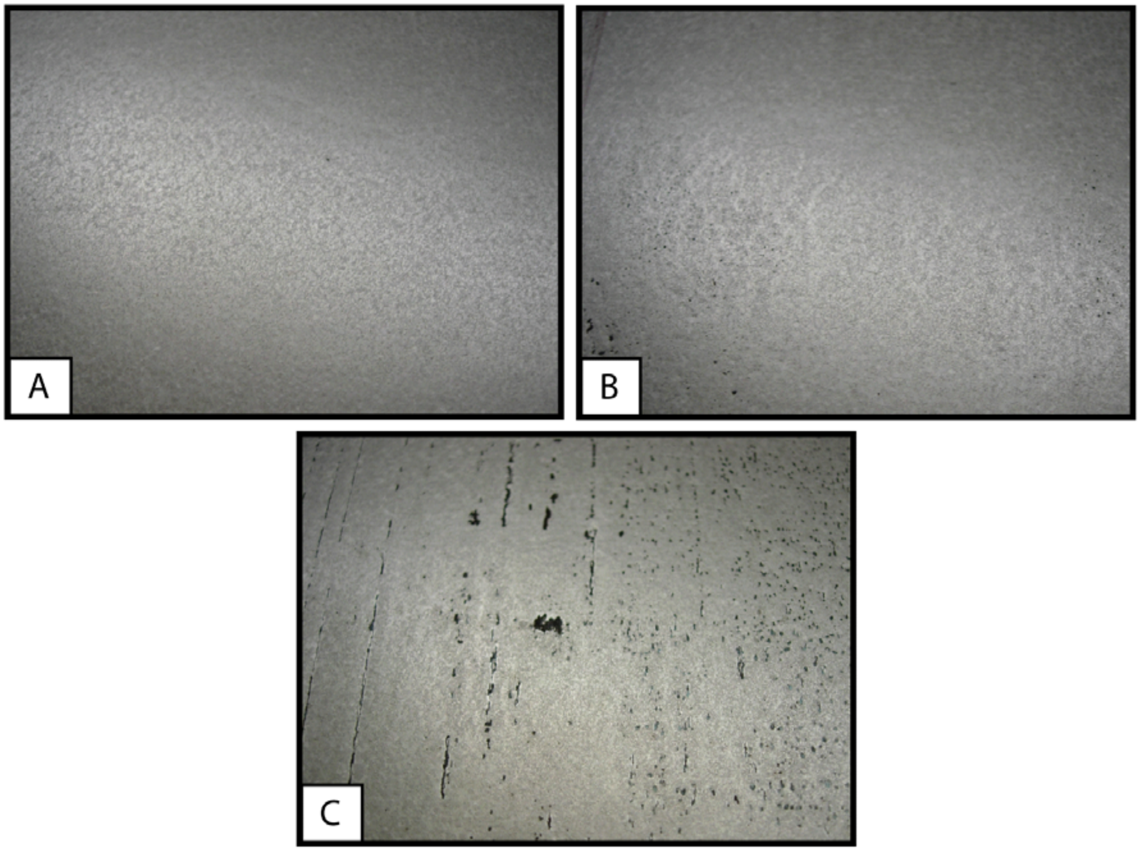

Figure 6.2 Photographs of typical defect free (A), pinhole uncoated (B) and gross uncoated (C) hot dip metallic coatings.

In accordance with the findings presented in Chapter 4, the metallic coating quality results outlined above suggest that the use of triglyceride-based sulfurised EP additives (sulfurised triglycerides) in commercial cold rolling oil formulations causes the formation of uncoated defects. Oils 560350, N609DPD, XR81628 and XR81629 all contain sulfurised triglycerides in the concentration range 3-20 % w/w (0.3-0.6 % w/w sulfur) and produce metallic coatings which contain pinhole through to gross uncoated defects. Removal of the sulfurised triglyceride from oil 560350 to give oil 560350noS results in a defect-free coating, confirming that sulfurised triglycerides, as opposed to other sulfur-containing ingredients contained in the oil formulation such as mineral oil/corrosion inhibitor, are responsible for uncoated defect formation. Similarly, increasing the sulfurised triglyceride concentration of an oil increases the uncoated defect severity; oil XR81627 contains no sulfur and gives rise to a defect-free coating, whilst oils XR81628 (0.3 % w/w sulfur) and XR81629 (0.6 % w/w sulfur) result in the formation of medium to pinhole uncoated and gross uncoated defects respectively. The coating results obtained for oil BSLWP1.1 verify the conclusion reached in Chapter 4 that sulfurised additive chemical structure plays an important role in determining metallic coating quality; the BSLWP1.1 formulation contains 0.4 % w/w sulfur in the form of TPS 20 but does not give rise to uncoated defects.

The utility of phosphorus- as opposed to sulfur-based EP additives is highlighted by the coating results obtained for oils CAT 29, 560453, BSLWP1.1, and U1388501. These formulations contain phosphorus-based EP additives in the concentration range 0.4-0.8 % w/w (0.02-0.04 % w/w phosphorus) and produce defect-free metallic coatings. The presence of uncoated defects in the XR82154-treated sample suggests that other lubrication additives can interfere with hot dip metallic coating quality; XR82154 is unique as it contains a mixture of polyester, di-carboxylic acid and phosphorus-based EP additives.

Finally, the metallic coating quality results obtained for oil SB4198 appear to contradict the findings made in Chapter 3. The SB4198 formulation contains ~ 30 % w/w base ester B (a highly unsaturated synthetic ester which gives rise to more uncoated defects than comparatively saturated base esters A and C) and yet it produces a defect-free metallic coating. This result could be due to high anti-oxidant levels preventing ester oxidation reactions and thereby minimising the formation of problematic residues.

6.3.2 Oil Residue Formation by PDSC and TGA

Continuous heating PDSC and TGA analysis of the oil formulations was performed and the values of four key parameters, the % residue at 500 ^{o}C, the % B/A ratio, T_{max} secondary region and T_{end}, were evaluated (refer to table 6.1).

The data obtained by PDSC show that the T_{max}, % B/A ratio and T_{end} values determined for the oils range between 380.3-421.6 ^{o}C, 4.22-32.7 % and 478.4-499.8 ^{o}C respectively.

Oils XR81627 and BSLWP1.1 produce defect-free metallic coatings and display the lowest parameter values by PDSC. Conversely, oils which produce greater levels of uncoated defects, such as 560350, N609DPD and XR82154, give higher PDSC parameter values, confirming that the PDSC parameters are associated with metallic coating quality.

The TGA data generally occur over a narrower range suggesting that there is less variation in the thermo-oxidative mass loss process between different rolling oils. The T_{max}, % B/A ratio, T_{end} and % residue at 500 ^{o}C values determined for the oils fall within the ranges 470.3-480.5 ^{o}C, 18.0-46.7 %, 508.8-541.1 ^{o}C and 1.20-3.80 % respectively. As observed by PDSC, oil XR81627 generally produces the lowest TGA parameter values. However, oils which perform badly according to the PDSC data produce varying TGA parameter results. For example, oil N609DPD gives one of the highest PDSC % B/A ratio values at 27.3 %, however by TGA it produces the lowest % residue at 500 ^{o}C (1.20 %) but the highest T_{end} (541.1 ^{o}C). These observations imply that the cause behind uncoated defect formation varies between oils and can be related to the formation of residues that cause a significant change in steel surface chemistry (as indicated by the PDSC % B/A ratio) as well as large amounts of surface residue (measured by the TGA parameters).

The PDSC and TGA data also show that parameter values are associated with oil composition. The results obtained for oils 560350 and 560350noS indicate that removal of the sulfurised triglyceride additive causes a significant reduction in the % B/A ratio (30.6 → 18.5 %) and T_{end} (493.7 → 479.4 ^{o}C) values by PDSC. However, there is no significant effect on the TGA and PDSC T_{max} values (420.3 ^{o}C ~ 421.6 ^{o}C) or the TGA % B/A ratio (36.4 % ~ 34.0 %), T_{end} (508.8 ^{o}C ~ 514.2 ^{o}C) and % residue at 500 ^{o}C (1.46 % ~ 1.30 %). Similarly, oil XR81628 displays higher parameter values than oil XR81627, confirming that the 10 % w/w sulfurised triglyceride contained in oil XR81628 alters the chemical nature of the residue formed by the thermo-oxidative decomposition process and increases the amount and thermal stability of this residue. The fact that more TGA and PDSC parameters are influenced by the presence of a sulfurised triglyceride additive in the XR81628 oil than the 560350 oil could be due to the increased formulation complexity of the 560350-based oils; high levels of residue and increased residue thermal stability in oil 560350noS could be caused by the presence of other additives. There is little difference between the PDSC and TGA parameter values obtained for oils XR81628 and XR81629 other than the PDSC % B/A ratio (21.0 → 30.3 %), suggesting that further increases in the sulfurised triglyceride concentration only alters residue chemical composition. These findings are in agreement with those in Chapter 4, where increasing the sulfurised triglyceride concentration in a base ester/sulfurised triglyceride blend caused an increase in the PDSC % B/A ratio but had little effect on the TGA % B/A ratio at sulfur concentrations below 5 % w/w.

6.3.3 Relationship Between Oil Residue Formation and Metallic Coating Quality Results

In order to rank the oils according to each of the TGA and PDSC parameters, the values shown in table 6.1 were normalised according to equation 6.1 below:[19]

$$X_{normalised} = \frac{X_{sample} - X_{lowest}}{X_{highest} - X_{lowest}} \qquad \text{Equation 6.1}$$

where X = % residue at 500 ^{o}C, % B/A ratio, T_{max} or T_{end}.

The normalised values for each of the oils are presented in table 6.2. The oil formulations are coded in the same manner as for table 6.1 and the normalised parameter values are coded such that oils producing the seven lowest values for each parameter are light grey, oils with the eighth to eleventh lowest values for each parameter are mid grey and the oil with the highest value for each parameter is dark grey. Where the order of the normalised parameter coding corresponds to the coding of the oil formulations with respect to metallic coating quality, the normalised parameter values predict metallic coating quality.

Table 6.2 Summary of the normalised TGA and PDSC parameter values and combined metallic coating quality indices (CI, PI and TI) for the twelve rolling oil formulations.

= defect-free = medium / pinhole-uncoated = gross-uncoated

Oil Formulation	PDSC			TGA				Comprehensive Index (CI)	PDSC Index (PI)	TGA Index (TI)
	T_{max} (^oC)	% B/A ratio	T_{end} (^oC)	T_{max} (^oC)	% B/A ratio	T_{end} (^oC)	% Residue at 500 ^oC			
XR81627	0.000	0.000	0.252	0.000	0.000	0.186	0.138	0.58	0.25	0.32
BSLWP1.1	0.913	0.688	0.000	0.863	0.527	0.269	0.127	3.39	1.60	1.79
560453	0.838	0.495	0.369	0.608	0.757	0.458	0.577	4.10	1.70	2.40
560350noS	1.000	0.502	0.047	0.706	0.559	0.167	0.038	3.02	1.55	1.47
U1388501	0.724	0.664	0.621	0.765	0.818	0.498	0.769	4.86	2.01	2.85
SB4198	0.167	0.006	0.645	1.000	0.552	0.464	0.808	3.64	0.82	2.82
CAT29	0.862	0.492	0.991	0.843	0.604	0.053	0.865	4.71	2.34	2.36
N609DPD	0.833	0.810	0.729	0.647	0.677	1.000	0.000	4.70	2.37	2.32
560350	0.969	0.929	0.715	0.725	0.643	0.000	0.100	4.08	2.61	1.47
XR82154	0.661	1.000	1.000	0.598	1.000	0.331	1.000	5.59	2.66	2.93
XR81628	0.874	0.590	0.939	0.471	0.690	0.421	0.923	4.91	2.40	2.50
XR81629	0.879	0.916	0.949	0.549	0.963	0.285	0.869	5.41	2.74	2.67

Table 6.2 shows that the sequence of the oils with respect to the individual normalised parameters does not correspond to the oil sequence with respect to metallic coating quality so that no single PDSC or TGA parameter is capable of predicting oil impact upon metallic coating quality. For example, the normalised PDSC T_{max} value determined for oil 560350noS (1.000) suggests that 560350noS produces gross uncoated defects when the metallic coating quality results in table 6.1 show that 560350noS gives a defect-free coating. Similarly, the TGA T_{max} values obtained for oils N609DPD, XR82154, XR81628 and XR81629 imply that these oils produce defect-free metallic coatings when the table 6.1 results show that they produce medium to pinhole through to gross uncoated defects. Although the TGA % residue at 500 ^{o}C and PDSC % B/A ratio and T_{end} parameters reflect the metallic coating quality data more accurately, false positives and negatives are still apparent. These inconsistencies arise because the formation of uncoated defects in 55Al-43.4Zn-1.6Si is dependent upon both the amount of residue formed by oil decomposition as well as the chemical nature of this residue such that oils which decompose to leave small amounts of residue can still cause uncoated defects. In order to account for these effects and more accurately predict oil impact upon metallic coating quality, three indices combining multiple TGA and PDSC parameters were developed: a comprehensive index (CI) equivalent to the sum of all the normalised TGA and PDSC parameter values; a PDSC index (PI) equivalent to the sum of all the PDSC parameter values, and a TGA index (TI) equivalent to the sum of all the TGA parameter values. The sequences of the oil with respect to the CI, PI and TI indices are shown in table 6.2.

As for the discrete TGA and PSDC parameters, the CI and TI indices fail to accurately reflect the sequence of the oils with respect to metallic coating quality. This could be due to the TGA data reflecting a combination of oil volatilisation and residue-formation effects, the former of which may not impact upon metallic coating quality; oil and/or oil decomposition product evaporation at high temperatures does not necessarily cause significant amounts of residue to form or alter the steel surface chemistry. Furthermore, the narrow range over which the TGA parameters values occur reduces the effectiveness of the CI and TI indices in accurately distinguishing between oils. However, the sequence of the oils according to the PI index clearly matches that determined by the industrial metallic coating test results; oils giving rise to defect-free coatings produce lower PI values than oils which produce medium to pinhole uncoated and gross uncoated defects respectively. On the basis of these results, oils with a PI index between 0 and 2 produce defect-free coatings, oils with a PI index of greater than ~ 2 produce medium to pinhole uncoated defects and oils with an index value above 2.6 produce gross uncoated defects. The PI index can therefore be used to screen rolling oil formulations according to the level of uncoated defects they produce.

6.4 Conclusions

The effect of twelve commercial cold rolling oil formulations on 55Al-43.4Zn-1.6Si hot dip metallic coating quality has been assessed. The oils have been graded into three categories according to the level of uncoated defects they produce; defect-free, medium to pinhole uncoated and gross uncoated. The metallic coating quality results confirm findings in Chapters 4; triglyceride-based sulfur EP additives give rise to uncoated defects whereas phosphorus-based additives do not. The detrimental impact of ester unsaturation levels on uncoated defect formation was not substantiated due to the presence of anti-oxidant additives. Four TGA and PDSC parameters indicative of oil residue formation characteristics (the % residue at 500 ^{o}C, % B/A ratio, secondary region T_{max} and T_{end}) were selected to form the basis of a predictive test to gauge oil impact on metallic coating quality. The results show that no single parameter is capable of predicting metallic coating quality although the % residue at 500 ^{o}C and PDSC % B/A ratio parameters gave the best results. Consequently, three indices combining multiple TGA and/or PDSC parameters, CI, PI and TI, were evaluated. 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. Oils with a PI value between 0 and 2 produce defect-free coatings, those with PI values greater that 2 but less that 2.6 produce medium to pinhole uncoated defects and oils with PI values greater than 2.6 produce gross uncoated defects. The PI index therefore constitutes a rapid method via which new rolling oil formulations can be screened to compare their likely impact upon hot dip metallic coating quality.

6.5 References

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