

Contribution of the Magenta Pigment to Calcium-Induced Piling in Web Offset Lithography

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Abstract

It is known that one of the many factors promoting the formation of piling is the presence of calcium ions. Besides calcium carbonate filler, one of the potential sources of these detrimental ions is the Lithol Rubine molecule present in the magenta ink. Our objective was to determine the effect of chemical conditions on the potential contamination of the blanket and the wetting solution system by calcium ions present in the magenta pigment.

We have used an ion selective electrode to measure the release or uptake of calcium by Lithol Rubine at different pH values and at different ionic strengths. The objective being to try and recreate the same conditions present in a web offset press. We have used a conductometric titration protocol to determine the amount of both carboxylic and sulfonic acid groups present in the Lithol Rubine sample. We have also characterized impurities that could interfere with the ion selective electrode using ICP-OES and the potential presence of free calcium ions.

Results indicated that as the pH was lowered, the amount of free calcium in Lithol Rubine solutions was rising. The effect of the ionic strength was more complicated: release or uptake of calcium have been observed depending on reaction time. Based on these results, we have concluded that high ionic strength and low pH conditions could promote the dissociation of the Lithol Rubine-calcium complex and the formation of deposits on blankets and in the wetting solution system.

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Introduction

Piling, which is defined as a buildup of unwanted material on the surface of a lithographic blanket, is a significant problem for many web offset printers. It is known that one of the many factors promoting the formation of piling is the presence of multivalent ions. These ions, in particular calcium, play an important role in the formation of insoluble precipitates which can lead to piling on blankets. There are many potential sources of calcium ions in the offset process. The most obvious one being the calcium carbonate used as filler in some supercalendered paper grades. However, there are also some other sources that need to be studied more closely. Among them, one potential candidate is the magenta pigment which contains two types of calcium ions:

- Structural calcium which is an integral part of the structure of the pigment.
- Excess free calcium which comes from the conversion of the pigment from the protonated to the calcium form.

As it can be seen from Figure 1, the magenta pigment, also called Lithol Rubin, is the calcium salt of 3-hydroxy-4-[(4-methyl-2-sulfo)phenyl]azo]-2-naphthalene carboxylic acid. It contains two acidic groups, a sulfonic acid and a carboxylic acid, that are neutralized by a calcium ion.

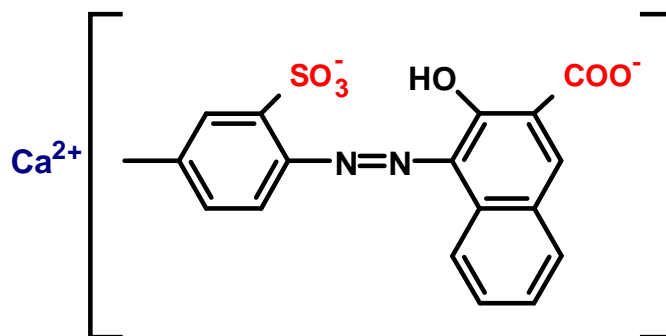


Figure 1. Chemical structure of Lithol Rubin, the magenta pigment (3-hydroxy-4-[(4-methyl-2-sulfo)phenyl]azo)-2-naphthalene carboxylic acid calcium salt)

Even though it has already been suggested that the magenta pigment could release calcium under certain conditions, its effective contribution to the total amount of calcium in the offset process has not been clearly established yet.

Many factors like pH and ionic strength in the wetting solution system could have a significant effect on the amount of calcium ions released by the magenta pigment. Therefore, our objective was to determine the potential contamination of the blanket and the wetting solution system by calcium ions present in the magenta pigment.

Material and methods

Chemical used

The magenta pigment used in this study, Lithol Rubin BCA, was obtained from TCI America. It has a purity of 87,2% (determined by UV-Visible spectroscopy). The standard calcium solution (PlasmaCal 1000 µg/L) was obtained from SCP Science. The ionic strength of solutions was adjusted with either 0,1N NaCl for conductometric titrations or 4,0M KCl for all other experiments.

Free soluble calcium concentration and pH were measured with a Mettler Seven Multi pH / ion meter equipped with an ionic expansion unit and a Mettler DCA240-Ca calcium combination ion selective electrode (ISE).

Characterization of the Lithol Rubin sample

As it was mentioned earlier, a typical magenta pigment can contain structural and free excess calcium. The total amount of calcium in the pigment was measured by acidic microwave digestion of the pigment and ICP-OES analysis. The maximum amount of structural calcium was calculated from the number of acidic groups on the molecule as determined by conductometric titration. Free calcium, if present, could be calculated by difference.

The determination of the amount of carboxylic and sulfonic acid groups in the pigment was measured by conductometric titration using a similar method to the one developed by Katz et al. (1984) for the titration of pulp samples. The method is based on the relative strength of carboxylic and sulfonic acids.

Release of calcium: Effect of pH and ionic strength

It is well known that the potential difference measured between a reference electrode and an ISE is related to the activity of the ion of interest and not to its concentration. In consequence, changing the ionic strength of a solution will change the response of an ISE to that solution even if the concentration of the measured ion, calcium in this case, remains the same. When taking

measurements at different ionic strengths, as it is the case in this study, one would have to standardize the membrane response at all ionic strength levels studied. To avoid this problem, we have first measured the ISE response to a standard Ca^{2+} solution with increasing ionic strength up to 0,1M. Then, we have measured the response of the same ISE to a Lithol Rubin solution in the same ionic strength range. By doing so, we have obtained two curves:

- ISE potential against ionic strength for the standard calcium solution
- ISE potential against ionic strength for the Lithol Rubin solution

By calculating the difference between the initial potential and any another point (*i*) on each curve, it is possible to measure the deviation of the ISE response for that particular point (*i*) for both the standard (ΔE_{Std}) and the Lithol Rubin (ΔE_{LR}) curves. The change in calcium ion concentration in the Lithol Rubin solution Δc_{LR} can then be calculated with the following equation:

$$\Delta c_{LR} = F c_{LR,0} \left(10^{\frac{\Delta E_{LR} - \Delta E_{Std}}{0,0296}} - 1 \right) \quad \text{where} \quad \begin{cases} F = \text{Dilution factor} \\ c_{LR,0} = \text{Initial Lithol Rubin conc.} \end{cases} \quad (1)$$

The mathematical development of Equation (1) is given in Appendix. Negative Δc_{LR} values indicate a reduction of the calcium concentration and an uptake of calcium by Lithol Rubin molecules while positive Δc_{LR} values indicate an increase of the calcium concentration or a release of calcium by Lithol Rubin molecules.

Results and Discussion

Before any experiments could be realized with the pigment, it was necessary to characterize it. The amount of calcium and the number of sulfonic and carboxylic acid functions in our sample were measured.

The total amount of calcium in the pigment, measured by ICP-OES, was found to be 7,65% w/w. This is much less than the 9,42% w/w theoretical value that is given by the mass fraction of calcium in the Lithol Rubin molecule. Several other metal ions have been analyzed. Among them, only sodium was present in significant concentration (1,1% w/w). The concentration of all other metals (K, Mn, Mg, Al, Fe and Cu) was below 100 ppm. Insoluble material, accounting for around 1,4% w/w of the sample mass, was also found after the acidic digestion

of the pigment. The amount of calcium found indicated that the pigment did not contain any excess calcium. Assuming that the remaining mass of the pigment was composed of divalent Lithol Rubin ions, there was even not enough calcium to neutralize all the negatively charged acidic groups.

Let's now turn our attention to sulfonic and carboxylic acids. These were measured by conductometric titration. Figure 2 shows the titration of protonated Lithol Rubin with sodium hydroxide. The curve is divided in three parts. The first descending line corresponds to the neutralization of the excess HCl added before the titration and to sulfonic groups. The horizontal line represents the neutralization of carboxylic acids and, finally, the ascending line shows the accumulation of sodium hydroxide after the endpoint of the titration. Making the required calculations, we found that the pigment contained 2,38 mmol/g of sulfonic acids and 2,22 mmol/g of carboxylic acids. These two numbers should have been equal since the molecule contained similar amounts of these two acids. Unfortunately, there was not enough data available to determine if the two results were significantly different. However, if we assume that the pigment is 87,2% pure, as it is claimed by the supplier, we obtain an experimental to theoretical ratio of 0,927 for calcium. This is in accordance with the ratio found for carboxylic acids (see Table 1). The amount of sulfonic acids was overestimated probably because of the presence of a small amount of another type of strong acid in the pigment. Table 1 summarizes results obtained for the characterization of the Lithol Rubin BCA sample used in this study.

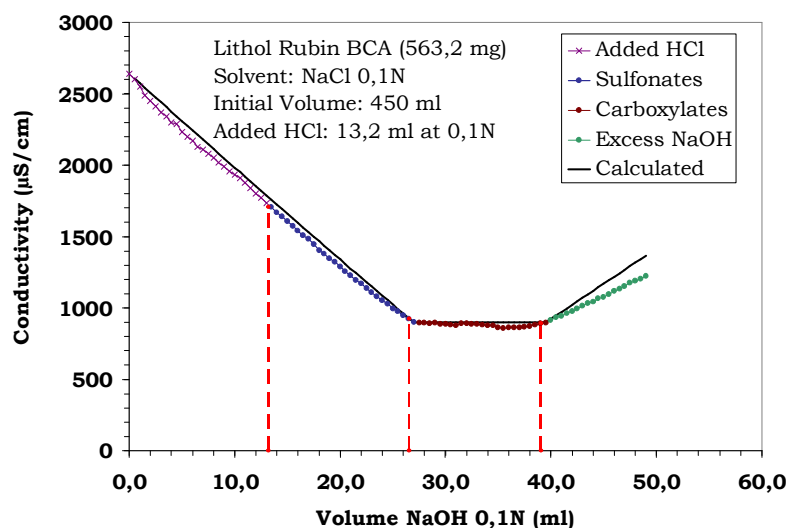


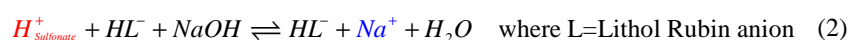
Figure 2. Conductometric titration curve of protonated Lithol Rubin with sodium hydroxide

To confirm that the observed changes in conductivity were really due to the expected neutralization reactions and accumulation of ions, a theoretical curve was computed and is shown as a solid black line in Figure 2. The total conductivity of a solution is a function of the molar conductivity and the molar concentration of each ion present. However, it is only necessary to take into account ions whose concentration should change after each addition of titrant to calculate the theoretical curve shown in Figure 2.

Table 1. Characterization of the Lithol Rubin BCA sample: Calculated and experimental chemical composition

	Calcium (% w/w)	Calcium Corrected for purity (% w/w)	Sulfonates (mmol/g)	Carboxylates (mmol/g)
Theoretical	9,42	8,22	2,36	2,36
Experimental	7,65	7,65	2,38	2,22
Exp. / Theo.	0,812	0,927	1,01	0,941

In the first part of the curve, the descending line, free H⁺ ions coming from either added hydrochloric acid or the dissociation of sulfonic acids are neutralized by the addition of sodium hydroxide. By calculating the expected change in concentration for each ion, it was possible to obtain the net change in conductivity after each addition of titrant. For the neutralization of sulfonic acids, and other strong acids which might be present in the pigment, the calculated value is -32,6 μS/cm and corresponds to the following reaction:



The experimental value we found was -32,3 μS/cm. For this first part, calculated and measured conductivity values are in good agreement.

The central horizontal line indicates that no change in conductivity occurs during the neutralization of carboxylic acids. In the original method developed for the titration of pulp fibers, this constant conductivity was explained by the fact that, as carboxylic acids are neutralized, sodium ions replacing hydrogen ions were immobilized near the fiber-water interface (where carboxylic acid groups are located). The same phenomenon seems to occur with Lithol Rubin. The divalent anionic form of the pigment acts like pulp fibers. Sodium ions are immobilized near the anion, probably between the two acidic groups, and cannot contribute to the total conductivity of the solution. The corresponding neutralization reaction can be expressed as:



Conductivity measurements in the horizontal part of the curve were very constant. The average value was 881 μS/cm with a coefficient of variation of only 1,4%.

Finally, in the ascending part of the curve, sodium hydroxide should accumulate in the solution. This should have given a conductivity increase of +24,5 μS/cm with each addition of titrant. However, the experimental value was only +17,1 μS/cm. The smaller increase could be attributed to calcium hydroxide precipitation at high pH values (higher than 10) that were reached near the end of the titration.

In summary, the characterization of the Lithol Rubin sample showed that the pigment was around 94% pure on a weight basis. For calcium, this translates into a 87,2% w/w purity. The remaining mass was composed of unidentified organic and inorganic material. Finally, the pigment was well washed. We did not find any excess calcium.

Effect of pH

The effect of pH on the solubility of calcium is well known. Most of the work done on calcium release by the magenta pigment was based on the fact that as pH is lowered, calcium solubility in water increases displacing the equilibrium shown in Equation (4) to the right:



However, it is also important to take into account the time needed to reach a new equilibrium when pH is changed. As an example, when measuring the ISE response at low pH, it was necessary to wait for 30 to 45 minutes to reach a stable reading. However, as the pH increased, the equilibrium was reached much faster (within five minute). In general, the calcium concentration was overestimated when measurements were taken before equilibrium conditions. This problem will be discussed in more details in the next section.

Our results indicated that the effect of pH was as expected: as the pH lowered, the dissociation of Lithol Rubin increased resulting in a higher concentration of free calcium ions (Figure 3). Similar results were obtained by Braun (1985) for the acidic part of the curve (below pH 7). In our study, we have increased pH to higher values to determine the effect of neutral wetting solutions.

The ionic strength of the solution that was used to obtain the curve shown in Figure 3 was adjusted to 0,08M. In consequence, the addition of titrant (sodium hydroxide) did not influence significantly neither the ionic strength of the solution nor the response of the ISE.

Between pH 7 and 10, the maximum calcium concentration is controlled by the solubility of calcium hydroxide ($Ca(OH)_2$) since no other precipitating cations are present. In a real wetting system, other anions that can cause the precipitation of calcium are present (e.g. citrates, phosphates). The increase in calcium in this range is explained by the fact that the total concentration of free Ca^{2+} is lower than that of calcium hydroxide. The sudden increase in free calcium at pH 7 may be caused by the important increase in calcium solubility near this pH value. At pH 7, 65% of the total calcium has already been released from Lithol Rubin. The remaining calcium was slowly released as the pH was further lowered.

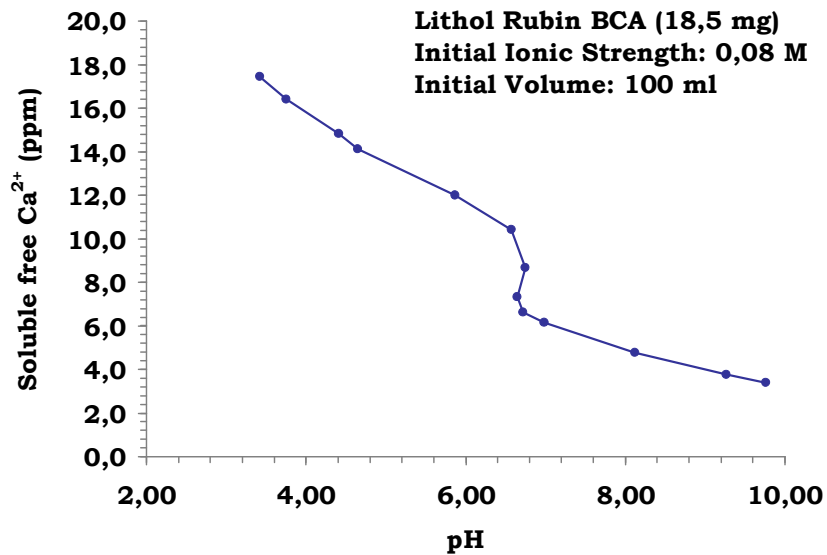


Figure 3. Calcium release from Lithol Rubin with pH

Effect of ionic strength

The variation of the calcium concentration with ionic strength was calculated with Equation (1). Results are shown in Figure 4. Two different Lithol Rubin concentrations have been studied: 22 ppm and 70 ppm. It is important to note that different stabilization times were used for each concentration. In the case of the 70 ppm solution, which was first obtained, the stabilization time was relatively short (15 minutes) between additions of ionic strength adjuster. The pH was relatively stable along each experiment. For example, in the case of the 70 ppm curve, the pH went from 5,0 to 6,1. According to Figure 3, the calcium release in that pH range should be less than 10% of the total calcium available. Variations observed in Figure 4 are much larger than that value. In consequence, these variations really represent the effect of ionic strength.

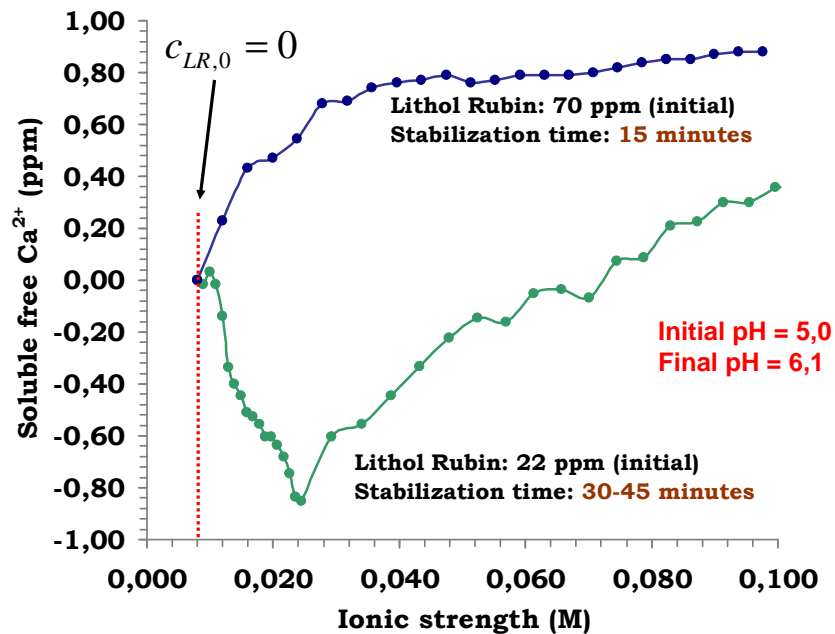


Figure 4. Effect of ionic strength on calcium release or uptake by Lithol Rubin at two different concentrations

It was also relatively difficult to measure the initial calcium concentration of both standard and Lithol Rubin solutions. The initial calcium concentration of Lithol Rubin solutions ($c_{LR,0}$), which appears in Equation (1) above, was required to calculate the variation of the calcium concentration in these solutions. Because of this problem, the value of $c_{LR,0}$ was arbitrarily set to 0 at an ionic strength of 0,008M. In consequence, concentrations shown in Figure 4 are not actual concentrations. The amount of calcium that was initially present in solutions was ignored. This explains the presence of negative concentrations.

For the 70 ppm solution, a 15 minute stabilization time was used. Under these conditions, calcium was gradually released from Lithol Rubin at the lower ionic strength until a stable concentration was reached. In the case of the low Lithol Rubin concentration (22 ppm), much longer stabilization times (30-45 minutes) were used. Under these conditions, a different behavior was observed. Very low ionic strength prevented calcium dissociation, calcium uptake was observed. However, at higher ionic strength, the trend was reversed and a release of calcium was observed. Unlike the 70 ppm curve, the 22 ppm curve did not level off, at least below 0,1 M ionic strength. This means that more calcium could be

released at higher ionic strength. We could not propose any theoretical explanation for the minimum observed on the 22 ppm curve.

Conclusions

The potential contamination of the blanket and the wetting solution system by calcium ions present in the magenta pigment was evaluated. The effect of pH and ionic strength on the release or uptake of calcium by a Lithol Rubine sample has been determined. A conductometric titration combined with ICP analyses showed that the pigment used in this study contained approximately 94% Lithol Rubine and no excess calcium. ISE measurements showed that high ionic strength and low pH conditions, which are frequently present on web offset commercial presses, promote the dissociation of the Lithol Rubine-calcium complex. Even though the time needed to reach equilibrium between variations of pH and ionic strengths was relatively long, especially at lower pH and ionic strengths, the magenta pigment could constitute a significant source of calcium. The presence of anions forming insoluble compounds with calcium on a real offset press would accentuate the release of calcium. In conclusion, the magenta pigment can certainly promote the formation of deposits on blankets and in the wetting solution system.

Acknowledgments

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Literature cited

Braun, F. E.

Studies of offset inks – The effect of pigments on the formation of emulsions, *Am. Ink Maker* 63(2):26-48 (1985).

Katz, S., Beatson, R.P. and Scallan, A.M.

The determination of strong and weak acidic groups in sulfite pulps, *Svensk Papperstidning* 87(6):R48-R53 (1984).

Appendix

The ion selective electrode used in this work is a membrane electrode that is permeable to calcium ions. The potential across the membrane is given by the Nernst equation:

$$E = \frac{RT}{zF} \ln \left(\frac{\gamma_A c_A}{\gamma_B c_B} \right) \quad (\text{A1})$$

Where A refers to calcium ions in the bulk solution and B refers to calcium ions in the membrane inner solution. In the case of calcium ISE, calcium ions activity inside the membrane is constant so $\gamma_B c_B$ is a constant. Keeping the ionic strength below 0,1M, we can use the Debye-Huckel equation to calculate the activity coefficient of calcium ions in the bulk solution (γ_A) leaving only the calcium concentration unknown. Therefore, the potential difference (ΔE) between initial conditions ($\gamma_0 c_0$) and a certain addition of ionic strength adjuster ($\gamma_i c_i$) at standard temperature and pressure is given by:

$$\Delta E_i = 0,0296 \times \log \frac{\gamma_i c_i}{\gamma_0 c_0} \quad (\text{A2})$$

The difference between ΔE_i values for a standard Ca solution and a Lithol Rubin solution of similar ionic strengths can be expressed as:

$$\Delta E_{i,LR} - \Delta E_{i,Std} = 0,0296 \times \log \left(\frac{\gamma_{LR,i} c_{LR,i}}{\gamma_{LR,0} c_{LR,0}} \times \frac{\gamma_{Std,0} c_{Std,0}}{\gamma_{Std,i} c_{Std,i}} \right) \quad (\text{A3})$$

In the case of the standard calcium solution, we are adding known amounts of ionic strength adjuster to a solution of known initial concentration in Ca^{2+} . In consequence, the calcium concentration of the standard solution can be calculated with:

$$c_{Std,i} = \frac{V_0}{V_0 + V_{ISA}} c_{Std,0} = F c_{Std,0} \quad \text{where } F = \text{dilution factor} \quad (\text{A4})$$

Some simplifications can be done to Equation (A3): $\gamma_{LR,0}$ and $\gamma_{Std,0}$ are equal to 1 since they are measured a solution with an ionic strength close to 0. We can also assume that $\gamma_{LR,i}$ and $\gamma_{Std,i}$ are similar at any ionic strength. Substituting

$c_{Std,i}$ with Equation (A4), applying those to Equation (A3) and rearranging to isolate $c_{LR,i}$:

$$c_{LR,i} = Fc_{LR,0} 10^{\frac{\Delta E_{i,LR} - \Delta E_{i,Std}}{0.0296}} \quad (A5)$$

We know that the calcium concentration in the Lithol Rubin solution during the titration ($c_{LR,i}$) will be equal to the initial concentration (adjusted for the dilution factor) plus the amount released or taken up by Lithol Rubin Δc_{LR} :

$$c_{LR,i} = Fc_{LR,0} + \Delta c_{LR} \quad (A6)$$

It is important to note that no calcium precipitation occurs at the studied pH values. Substituting Equation (A6) in Equation (A5) and solving for Δc_{LR} :

$$\Delta c_{LR} = Fc_{LR,0} \left(10^{\frac{\Delta E_{i,LR} - \Delta E_{i,Std}}{0.0296}} - 1 \right) \quad (A7)$$

This last equation is valid because when $\Delta E_{LR} - \Delta E_{Std} = 0$, we obtain $\Delta c_{LR} = 0$. It is also important to note that even if $c_{LR,0}$ is not measured accurately, only the absolute value of Δc_{LR} will be affected. The negative or positive sign associated to the value will still indicate accurately the release or uptake of calcium by Lithol Rubin.