CHEMICAL ADDITIVES FOR WARM MIX ASPHALTS

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ABSTRACT

Recently, new technologies have been developed to reduce the environmental impact of the road construction industry. Among them, the technologies that allow a substantial reduction on the energy consumed during the production of hot asphalt mixtures have taken a very important role. There are several technologies, based on very different physicochemical phenomena that allow producing what is now known as warm mix asphalts.

The work presented here describes the use of one particular type of warm mix asphalt technology based on chemical additives. This technology has been already proven to work under very different laboratory and field job conditions. It is based on the use of surfactant-type additives that enhances the workability of an asphalt mix allowing it to be paved and compacted at lower temperatures. Only a low concentration, from 0.2 to 0.5wt% with respect of bitumen, is required to have the desired effect.

The several advantages observed by the use of this warm mix asphalt technology are presented in this work, including field job examples, measured energy consumption reductions and environmental measurements.

It is also a matter of this work the discussion of the enhanced functionality that this particular kind of additives may provide. Examples of such are their role as adhesion promoters in the asphalt mixture and as aids on the incorporation of higher amounts of reclaimed asphalt pavement.

1. INTRODUCTION – WARM MIX APSHALTS

The term warm mix asphalts (WMA) has been given to those asphalt mixtures that are produced and paved at lower temperatures to those normally used in standard hot mix asphalts (HMA). During the last years, there has been an important development on the different technologies that allow such reduction of temperature and on the characterization of the resulting pavements. Currently, there are more than 20 different technologies that allow the production of WMA [1]. These techniques actually depend on very different physical and chemical processes to allow the production of WMA. The main challenge is to enhance the workability of the asphalt mixture as the temperature is reduced. As the temperature is reduced, the bitumen increases its viscosity making the covering of the agaregates and the compaction of the mix more difficult [2].

The several WMA technologies on the market can nevertheless been grouped on four categories, based on the physical principle used for enhancing the workability of the mixture at reduced temperatures:

Sequencing of hard and soft bitumens – One of the first technologies developed for WMA production was the one developed by Kolo Veidekke [3]. In this technique, sequential mixing of a portion of the aggregates with a hard bitumen is done before the rest is mixed with a foamed softer bitumen. This approach requires a substantial modification of the production plant (as it is actually a different process) and handling of different binders.

Water foam processes – This is a large group that includes probably the majority of WMA technologies on the market. In all of them, bitumen foam is produced by evaporation of water during the mixing process. The water vapour produced when in contact with the hot bitumen increases the surface area of the binder as well as provides additional energy to the system to better cover the aggregates. It is claimed by some technology providers that the amount of residual water (in liquid or vapour form) is key to maintain the workability of the mix afterwards. The main difference between the technologies in this group is the way the water and the binder contact takes place. One option is to add mineral additives that contain water to be released only at higher temperatures (as those used for asphalt mix production), an example of such additives are the zeolithes [3,4]. A different option is to produce the foam at the same time the bitumen is injected into the mixer. Such technologies are based on the actual machine (nozzle system) that can effectively generate the foam at such point of the mix production [5]. Another option is to only partially dry a portion of the mineral formula before adding the binder [6]. Such approach has the potential to reduce even further the temperature of production (as it may be below 100°C). However, the control of the amount of water present of the aggregate fraction, being key to the process, may be challenging. On last example of the foaming approach is to actually use a bitumen emulsion, instead of a dry binder. In this case the water is already in close contact to the bitumen when in contact with the heated aggregate [7].

Waxes – In this case, an additive is added into the bitumen to reduce its viscosity at mixing temperatures only. This has been achieved through the use of waxes [3,4]. The waxes are chosen such that they melt above about 100-110°C. On the melt state, they can decrease the viscosity of the bitumen, improving the bitumen covering of the aggregates and the workability of the mixture. At lower temperatures, they crystallize, reinforcing the bitumen at application conditions. They are usually used at concentrations of about 2 to 3% by weight of the binder. Care should be taken, not to work at temperatures lower than the crystallization temperature of the wax. These additives do modify the properties of the

bitumen, in particularly the low temperature properties [8], and could actually change its grade.

Chemical additives – On this group we found additives that act on a very different way than the before-mentioned wax additives. Contrary to waxes that modify the bulk of binder, the chemical additives act only at the interface between the mineral aggregate and the bitumen [9]. This is the reason why these additives actually are used on very small doses (from 0.3% to 0.6% by weight with respect of binder).

The reported benefits of WMA had been also subject to several previous publications [1,3,9]. There are several benefits as a consequence of reducing the temperature of an asphalt mix production. These advantages are mainly the reduction on energy used in the production and the reduction of the emissions related to this reduction in temperature. Other advantages such as the comfort to the workers can also be cited. However, some advantages are unique to each technology since they are the results of the particular mechanisms to achieve the reduction in temperature

In this work, a further discussion about the chemical additives is done. The properties of the asphalt binder comprising the additives as well as on the asphalt mixture are presented. The observed advantages by the use of the chemical additives, both those related to the reduction in temperature as well as those unique to the chemical additives are presented. The laboratory work and field jobs described and discussed in this work were carried out using a commercial additive patented by CECA, named CECABASE RT. These are liquid additives, which used at 0.3% to 0.5% by weight of the bitumen, are claimed to allow a reduction in asphalt mix production temperature of about 40°C [10]. More than 2.5 million tons of asphalt mix have already been produced around the world with these additives.

2. HOW CHEMICAL ADDITIVES WORK

The chemicals used for the production of WMA are actually surfactant-like molecules. As any surfactant molecule, they are capable of changing the interfacial interactions between two different phases. In this case the chemical additives interact at the mineral and bitumen interphase, changing the way the mineral interact between each other. A smaller amount of additive is required to cover the surface of the mineral aggregates than to actually change the properties of the whole volume of bitumen. This is the reason why such a small amount of chemical additive, between 0.3% and 0.6%, is required to produce WMA. At this small concentration of additive, even if it is a liquid with a lower viscosity than hot bitumen, the properties of the bitumen remain mainly unchanged. The viscosity and mechanical properties of the bitumen containing a chemical additive for WMA are not modified by its presence.

The viscosity as a function of temperature of a bitumen with and without a chemical additive for WMA was measured. A dynamical shear rheometer with temperature controlling capabilities was used to measure the viscosity at a shear rate of 100/s under a parallel-plate geometry. Figure 1a shows the viscosity curve of bitumen with a penetration grade of 35/50 1/10mm containing 0.3% of Cecabase RT additive. On the same curve, the viscosity of the original bitumen without the additive is also shown. It can be seen that the two curves are almost identical at the measured temperatures. Another measurement was carried out at lower temperatures to evaluate the effect of additives at normal use temperatures. The parameter G*/sin δ was measured using the same rheometer at a frequency of 2 Hz and 1% strain as a function of temperature between 20 and 100°C.

Figure 1b shows the curves of the 35/50 1/10mm bitumen with and without the chemical additive. It can be seen that the two curves superpose each other, demonstrating that there is practically no change on the bitumen rheological properties under the conditions of the test. If the high temperature performance grade criteria (PG–grade) is used as a guide line, the temperature at which the reference bitumen reach 1 kPa is 53.6°C. For the same bitumen with the additive, this temperature is 53.1°C. This difference is within the 2% error interval of the measurement, and could hardly change the attributed grade of the bitumen.

Figure 1 - Rheological measurements of a 35/50 1/10mm bitumen with and without a chemical additive for WMA.

These results confirm those published before where no significant changes in penetration values and ring and ball temperatures were observed when similar additives were used [11,12]

Bitumen is naturally a good adhesive on the aggregates, which is also the reason why it is used for pavement construction. This adhesion limits the movement and flow between the bitumen and the minerals during the production and laying operations, while playing an important role at application temperatures by increasing the overall material cohesion. Bitumen in an asphalt mix is spread and confined by the mineral aggregates during mixing. This can be observed on Figure 2a that shows a scanning electron microscope image of a cross section of an asphalt mix at edge of a large aggregate [9]. It is not difficult to imagine that the friction generated by all the interfaces between bitumen and aggregates is very high, which sets and controls the limits of the mixing, handling and compacting ability of the asphalt mixture. This is one of the reasons why it is necessary to work at relatively high temperatures for asphalt mix production in order to overcome this friction limitation.

The chemical additives for WMA production compete with the bitumen at the aggregate interface and are adsorbed in its place at asphalt mix production temperatures (between 200°C and 100°C). These chemical additives reduce the surface tension of the bitumen/aggregate interface during the mixing operation. Thus making easier for the bitumen to wet and finally cover the mineral aggregate even at lower mixing temperatures, where the bitumen has a higher viscosity (schema in Figure 2b).

More importantly, the additive helps to avoid a too strong bitumen adhesion on the mineral particles by acting as a lubricant during the mixing – handling – laying – compacting steps.

This effect is responsible for the improvement of the asphalt mix workability. At standard high temperatures, the use of the additive eases the whole industrial process (mixing – handling – laying – compacting steps). At reduced temperatures, about 40°C lower, the use of the additive enables to keep a good workability, comparable to that of a regular hot asphalt mix.

Figure 2 - a) Scanning electron microscope image of an asphalt mix cross section [9]. b) Scheme of the differences in surface tensions at the bitumen / aggregate interface, with and without chemical additives

Since, as mentioned above, the additive effect can only be evaluated when in contact of the mineral on an asphalt mix, the question raises of how to determine (or confirm) the effect of a chemical additive on the workability of the mix. The straight forward method is to carry out standard compaction experiments on the lab, at WMA temperature conditions, and see if they are comparable to those usually obtained at standard temperature conditions. This kind of testing is reassuring to a certain point, it can prove that WMA will perform on a similar way as a regular HMA, but it has been shown to have several limitations. One such limitation is its lack of sensibility to search for the optimal temperature, or conditions of WMA production. A research group published a study where they showed that by following the compaction of a mix by a Marshall press it was found that only a reduction of 10°C would be possible by using a chemical additive [11]. It is know from actual field experience than reductions in the order of 40°C are quite possible [9,12]. Another publication actually showed that the type of compaction could actually have an effect of the evaluation of WMA. It was found that the Marshall press was less adapted than the gyratory press for WMA studies [13].

Results from the compaction with the gyratory compactor of an asphalt formula for thin rolling courses (BBTM) are shown on Table 1. The formula contained 26% of a 0/2 fraction, 71% of a 6/10 fraction, 3% filler and 5.6% of polymer modified bitumen. The void percentage is calculated by the geometry of the sample after 40 gyrations under a pressure of 6 bar. The specimens were then tested under compress ion following NF P98-251-1.

Table 1 - Compaction of a BBTM formulation with and without the additive.

As can be seen in this case, the void content of the WMA with additives is closer to that of the HMA than that of the WMA without additives. The difference, however, is small and hardly significant. This suggests that simple compaction experiments, as mentioned before, might not be sufficient to characterize or search WMA conditions of a given formula. Nevertheless, more significant differences were observed on the indirect tensile strengths (ITS). The ITS for the non conditioned sample (stored dry for 2 days) actually showed a decrease in values for the WMA, probably due to the lack of cohesion of the sample. The WMA with the additive has a similar value to that obtained with the HMA.

The correct characterization of the WMA on the laboratory is an issue for all the WMA technologies since no standard test exists to evaluate the workability of a mix on the laboratory to this date. There are, however, several published techniques that attempt to evaluate the workability of an asphalt mix [14,15]. Some are based on actual torque measurements of the asphalt mixtures; other claimed that particular tribology measurements on the bitumen could actually be correlated to the workability of the final mix. Although the different tests have found a certain degree of success (differences observed between HMA and WMA), no method has been found to be fully representative to what is observed on the field.

On a previous paper, there were showed asphalt mix workability experiments carried out by the laboratory Baustofflabor Hamburg in Germany [12]. Their approach is also based on a direct torque measurement of asphalts mix. The resistance of a moving object inside the mix is measured as described in an official German publication [16]. The measured torque values actually increased as the mix was measured at a lower temperature (40°C lower). The measured values were 292 Ncm for the mix at 160°C and 318 Ncm for the mix at 120°C. When the measurement was carried out at the same conditions at 120°C with 0.5wt% of chemical additive in the bitumen, a value of 290Ncm was measured. This demonstrated that there was a significant effect of the additive, which brings back the torque value of a mix at 120°C to values comparable as those found at 160°C. These results further demonstrated the effect of chemical additives on the workability of asphalt mixtures, however, it would be somewhat difficult to widely implement this kind of measurements to the road community at large.

Another issue with the characterization of WMA on the lab is the obtained values of tensile strength. On some cases, the tensile strengths obtained from WMA are lower to those obtained with regular HMA, even at equivalent compaction levels. A possible explanation for this difference are the different levels of binder oxidation between a HMA and a WMA, which may result in a slightly softer mix in the WMA. Bitumen goes through a significant oxidation process during the mixing process. Since the oxidation process is a chemical reaction, with strong temperature dependent kinetics, bitumen at lower temperature should therefore be less oxidized. A previous publication has show differences between recuperated bitumens from HMA and WMA, where the WMA bitumen was softer [13]. It was also showed that originally the two bitumens, with and without chemical additive, did

not have this difference. This difference may be more pronounced in mixes containing soft bitumen, since the effect of hardening by the oxidation will be more accentuated.

To compensate this issue, some laboratories had actually suggested annealing the WMA from 2 to 4 hours, at the WMA temperature, before compaction (always within the limits of the norms) to better represent what is observed on the field [17].

3. ADVANTAGES OF WMA BY CHEMICAL ADDITIVES

The many advantages of WMA had been the subject of previous publications. Here some results from field jobs are presented to exemplify some of those advantages.

3.1. Energy and Emission reductions

The most direct consequence of reducing the production temperature of an asphalt mix is the decrease of the energy required for the process. This reduction of energy is directly related to the degrees of temperature reduced. From previous experiences the energy saving from a 30 to 40°C reduction of temperature goes between 20 to 35%. The amount of energy consumed is also related to other factors than just the temperature reduction. The production plant conditions and the aggregates humidity, for example, may strongly modify the amount of energy consumed.

Some WMA techniques, as mentioned before, depend on the presence of water on the aggregates to foam the bitumen [6]. Some of these techniques can actually have a stronger impact on the amount of energy consumed if the mix stay at temperatures below 100°C. Below 100°C the full evaporation of water is avoided, which results in a large energy saving (the latent heat of water is 2250 kJ/kg, quite large compared with it's heat capacity of 4.18 kJ/kgK). However, care should be taken to avoid potential problems with water moisture resistance.

Here below, an example of actual measurements of the energy consumed during the production of a thin rolling surface (BBTM in French) at HMA and WMA conditions is shown (Table 2). The amount of energy consumed showed is the average of several hours of production. The mix is regularly done at 170°C, as it is done with a polymermodified bitumen. By the addition of 0.4% of the chemical additive into the bitumen a reduction of 40°C was achieved.

Table 2 - Energy consumption on the production of a WMA

It can be seen that a significant reduction of the energy consumed (\sim 30%) is obtained by the reduction of 40°C in the production temperature.

An added benefit of reducing the production temperature can be an increase on the production rate. Since a lower temperature of the aggregates is needed, the burner output should be decreased (see Table 2). In addition to this, the production output may be increased so that the aggregates stay a shorter time on the heating drum, thus heating less. This is the case for the field job describe above. It can be seen that there is actually a slight increase in the production rate (9%) in addition to the reduction of the burner output. It should be noted that in some cases the control of the burner at very low outputs may be difficult and actually contrary to energy savings. A badly tuned burner at low outputs may work inefficiently, consuming a larger amount of fuel and producing more polluting emissions.

The emissions generated as a result of the production of an asphalt mix are also very sensitive to the temperature. An important source of the emissions generated during production are the combustion products of the fuels used to heat the aggregates. The reduction of these emissions is directly proportional to the decrease of production temperature of the mix. Another source of emissions are also those that may be directly produced by the bitumen at higher temperatures. In Table 3 measurements of the emissions generated at the production site during the same production of the thin rolling surface describe above are shown. The emission values are reported per ton of mix produced. The reductions on $CO₂$ and NOx (NO₂ equivalent reported on Table 3) emissions are close to that found for the energy consumption (-38 and –26% respectively). However, the effect of reducing the temperature has a higher impact on the total volatile organic components (TVOC) and the polycyclic aromatic hydrocarbons (PAH). Although the actual emissions values measured may vary according to the type of production plant, maintenance, etc... it is clear that there is an advantage when the temperature is reduced.

Additional measurements were also carried out during the paving operations to measure the quantity of VOC at which the workers are exposed. Three different locations were chosen to take the measurements for each of the HMA and the WMA paving operations. Detection instruments were placed on the driver of the compaction roller, on the driver of the paver and on a worker placed next to the paver. The detected amounts of VOCs were actually low, close to the detection levels for both cases, WMA and HMA. They were all well below the exposure limits dictated by the current legislation. There were however, differences between the measurements taken. As expected, the levels detected for the worker standing next to the paver were the highest, followed by those detected on the driver on the paver. The measurements for the driver of the compaction roller were the lowest. There were differences between the HMA and the WMA. The values measured in the WMA were between half and one third of those obtained in the HMA. For example, the naphthalene was present at 0.015 mg/m³ in the HWA for the worker next to the paver, while a value of 0.005 mg/m³ was found in the same conditions for the WMA.

Other advantage that results from the reduction of temperature, which is hard to evaluate, but easy to feel, during the paving operation is the comfort of the workers. It is more comfortable and safe to work with a mix at 130°C than with a mix at 170°C. The difference is even more noticeable when paving under hot weather conditions.

The emissions during the production and paving operation may not be the only potential sources of pollution. An experiment was carried out to detect if the presence of the chemical additive on the mix can eventually have an effect on the water that is in contact with it. Asphalt mix samples containing 0.5 wt% with respect of the bitumen of the Cecabase RT additive were stored in a closed container filled with water. The asphalt samples were only slightly compacted: enough to provide a shape to the sample but open enough to let the water fully penetrate into the mix. The water was then tested for toxicity under the European normative OCDE 201 that follows the growth of the water algae Pseudokirchneriella subcapitata to test ecotoxicity. Samples of the water were taken after three months and after one year. Additionally another set of samples were stored for the last 2 months of the year in an oven at 60°C. None of the water samples taken showed any toxicity (the growth of the algae was normal). This experiment shows that the addition of the chemical additive for WMA does not seems to have an effect on the toxicity of the asphalt produced with it.

3.2. WMA and Reclaimed asphalt pavement (RAP)

Another possible advantage of the WMA asphalts is the potential of increasing the amount of reclaimed asphalt pavement, RAP, which may be incorporated on the mix. The production process heavily controls the amount of RAP that may be added into a mix. Other than the final properties of the mix, the temperature of the virgin aggregates controls the amount of RAP to be used, since they provide the energy to heat the cold RAP. The temperature at which the virgin aggregates should be heated to heat the added RAP can be easily calculated from basic thermodynamics. It is basically a calculation of the heat given by the hot aggregates that is received by the cold RAP. Figure 3 shows the results of such calculation as the temperature that is required to heat the virgin aggregates to incorporate a given percentage of RAP in the formula. Two different situations are plotted: one where the mix ends up at a temperature of 160°C (such as in a standard HMA) and another where the final temperature is 120°C (WMA conditions). A water content of 4%, typical found in RAP, is taken into account since it has an important effect on the curves (need to evaporate this water). It should be noted that the relation between aggregate temperature and % RAP is not linear, since a larger amount of heat needs to be given at larger RAP contents by a lower mass of virgin aggregates, thus increasing their temperature even further.

Figure 3 - Calculated temperatures of virgin aggregates required to incorporate a given % of cold RAP.

From the plot it can be seen that there might be substantial advantages by the WMA for an increase amount of RAP. For example, it can be seen that a mix that is designed to incorporate 10% of RAP at 160°C may contain 15% more RAP while heating the virgin aggregates at the same temperature. Lets point out that the limit of the amount of RAP added may be physically limited by the temperature of the virgin aggregates. It can be can seen that to achieve 40% RAP, temperatures on the order of 300°C should be reached. Aggregates at these temperatures would burn the cold bitumen present in the RAP when they came in contact. This will decrease the quality of the final asphalt and may become a safety risk. Some techniques based on the bitumen foaming may become incompatible to those large temperature gradients.

Other that the actual production advantages as described above, there is the issue of the actual performance of the final mixtures at higher RAP contents. The problem that may be encountered is the lack of mix between the aged bitumen in the RAP and the virgin bitumen added, even it is of a softer grade to compensate. There is some discussion that the problem may actually be aggravated in WMA since the lower bitumen temperatures may do the incorporation of the aged bitumen even harder. Several studies should be carried out to understand the matter further.

An actual field job was recently carried out with the Cecabase RT additive where the RAP content was 30%. It was a surface layer originally designed to be done at 150°C. This field job was produced at 110°C and paved at 100°C. An amount of 0.3% of additive was added to the virgin 50/70 1/10mm penetration bitumen added into the formula (4% of virgin bitumen for a 5.3% of final bitumen content on the mix). The laboratory results: compaction in a gyratory press, moisture resistance (Duriez) and rutting of the mix were within the requirements. The field job was carried without problems and a good and homogeneous compaction was obtained. (Table 4)

Table 4 - Laboratory and field test results of a WMA with 30% RAP

The reduction of temperature of hot mixes that contain RAP can be successfully carried out with chemical additives. The possibility to further increase the amount of RAP incorporate should be subject of further studies to evaluate the impact not only on the production conditions but on the final properties of the mix as well.

3.3. Advantages Related to the chemical additives

Most of the advantages brought by the WMA mentioned above are actually achieved by the reduction in production temperature itself, rather than the actual effect of the chemical additive. There are however some additional advantages when chemical additives are used.

As described above, chemical additives for warm mix asphalts does interact at the mineral surface. Due to their chemical nature, they may actually also play the role of anti-stripping agents to improve the moisture resistance of the mixtures. Depending on the mix they may completely replace the use of an additional anti-stripping agent. For example, Table 2 shows the indirect tensile strengths of samples conditioned for 1 day at 60°C with and without chemical additive. It can be seen that the WMA sample with the chemical additive not only has a higher value that the reference WMA but also to the HMA. With the chemical additive for WMA a correct value of ITSR (> 75%) is obtained. In any case, for materials very sensitive to moisture damage, a low dosage of an additional anti-stripping agent may eventually be used in combination of the chemical additives for WMA to achieve a good moisture resistance performance.

Perhaps the largest advantage, unique to the liquid chemical additives, is that they are simple to use. No plant modification is required to use them. In any case, the addition of a pump that can dose the additive (very much as those used for the anti-stripping agents) might be needed. HMA and WMA may be switched between one another easily if an inline injection of the additive is used. Alternatively, the additives may also de added to the bitumen before the production of asphalt mix. They dissolve easily on the bitumen and may be stored in the bitumen for several days before their use.

The chemical additives mentioned in this work may be actually used at higher temperatures with no negative effects. It should be pointed that these are additives that improve the workability of the mix, which can be used to reduce the temperature for warm mix asphalt production. In fact, they might be used to add better workability to standard HMA, securing the job in case of delays or lower weather temperatures. The use of a chemical additive for WMA on a HMA can be also an extended transportation time. As discussed on a previous publication [12], the hauling time of the mix may be extended for about 3 times if it produced at HMA conditions with chemical additive and paving it at WMA conditions.

4. CONCLUSIONS

Several aspects about the use of chemical additives for WMA fabrication were discussed, including their mechanism, properties and advantages.

The chemical additives for WMA do not change the bitumen properties while improving the workability of the asphalt mixture. The viscosity and rheological behaviour of the binder remains practically unchanged. The additives only interact at the aggregate surface to modify and control the friction forces of the mix, thus requiring only a small amount (0.3- 0.6 wt% with respect of the bitumen) to have an effect.

The laboratory evaluation of the workability of the mix at WMA is challenging, however some information can be obtained from simple compaction experiments.

Energy savings and emissions reductions from an actual job had been shown. The advantages due to reducing the production temperature by means of a chemical additive were confirmed. No toxicity was found on asphalt mixtures containing the chemical additives when in contact with water for 1 year.

The possibility of increasing the amount of cold RAP, thanks to WMA was discussed. An example of an actual WMA field job with 30% RAP seems to support this thought.

Chemical additives for WMA may also play the role of anti-stripping agents as shown in here. Other advantages of liquid chemical additives that enhance the workability of the mix were discussed such as their ease of use without a plant modification and the possibility for longer mix hauling before paving.

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