Maintenance and Rehabilitation

New fluxing agent for Road applications

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Abstract

The context of this innovation is a will between two companies to create more sustainable roads without any compromise between efficiency and respect of the workers and environment. Fluxing agents are mainly used in road maintenance technics, and those additives are added in bitumen in large quantities, up to 20% in some cases. Today, fluxing agents can be categorized in 2 parts: • Efficient with strong labelling • Not labelled with limited efficiency. A new fluxing agent brings the best of both worlds: it has no label, and brings a high level of efficiency and versatility. The sustainability has been one of the priorities and the result speaks for itself: this additive has no toxic and ecotoxic classification and is biodegradable. So it is completely safe for the workers and the environment. Furthermore, fluxing agent global consumption can be decreased significantly, as the new solution is 20 to 45% more efficient, depending on the road technics considered. And last but not least, 45% of the raw materials are biosourced. The high efficiency observed is due to a high fluxing power, specific solubility in the bitumen, and narrow boiling range. All of these bring unique application properties (quicker cohesion build up, faster recovery of bitumen properties) with unique added value (less bleeding for surface dressing, extension of the application season for microsurfacing, higher durability of the cold mixes). On top of that, it is versatile as it can be used with all the road technics which use fluxing agents and various types of binders (pure and polymer modified bitumen in anhydrous or emulsion forms). 12 field trials have already been done during 2017 and 2018 in France, confirming the added value of this breakthrough additive. More field trials are about to come, with an expansion outside France: UK, US and Canada.

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1. INTRODUCTION

In the context of increasing scarcity of natural resources, disengagement of the State leading to under-funding and intensification of traffic, managing the road assets is a focus of concern for our society. Road maintenance is essential in order to preserve the road in its originally constructed condition and to protect adjacent resources and user safety. In the last decades, a lot of efforts have been made to improve the quality of road maintenance and its global footprint by developing and actively promoting new technics, almost always based on bituminous solutions. Despite its wide properties, bitumen shows some limits and additives are required to answer to the contractors 'need. Thus, the profession has been looking for new additives to take over today and tomorrow's challenges, a combination of efficiency and sustainability, and one broadly used in the maintenance paving techniques is fluxing agent. The main functionality of such product is to decrease temporarily the viscosity of the binder, in order to make the application easier: surface dressing, storable mixes or even cold mixes are mainly concerned. Another functionality of flux oil is to help the curing of bitumen emulsions, once applied on the road pavement.

2. NEW EFFICIENT FLUXING AGENT WITH OPTIMAL SUSTAINIBILITY PROFIL

Since the beginning of 2000, manufacturers and laying contractors can use 2 types of fluxing agents:

- Fluxing agents from distillation of petroleum and from petro chemistry, called mineral fluxing agents
- Fluxing agents from natural resources, such as methyl esters **[1][2],** called vegetal flux oils

Nowadays, mineral fluxing agents are widely used thanks to their level of performances, much higher than vegetal flux oils, well-known for their low efficiency causing disorders in some applications. These differences are mainly explained by their different way of action. Indeed, once the bituminous product, containing the fluxing agent, is applied on the road, the objective is that the bituminous binder gets back its original properties as quick as possible. For the mineral fluxing agent, the mechanism is quite simple as it is the evaporation: the narrower the distillation curve, the quicker the evaporation in the air and thus, the quicker the bitumen gets back to its original properties. This type of fluxing agent is qualified as "volatile fluxing agent". Concerning the vegetal flux oils, the mechanism is more complex: it is the additive itself, thanks to its specific structure, which reacts with the oxygen in the air, and then, enables to harden the bituminous product. This oxidation, called "siccativation" is very slow, and the cohesion build-up takes time which is not relevant compared to the short time required to reopen a road. Siccativant (oxidation) agents can be used to accelerate slightly the reaction but, it is not possible nowadays to control and stop this reaction: the hardening on the binder and thus, stiffness is observed on bitumen after a while, which lead to issue on some jobsite. Because of this mechanism, technical performances are limited for the vegetal flux oils.

Thus, the road pavement market is looking for greener, safer and more efficient technology to replace existing fluxing agent. Thanks to the collaboration of a road manufacturer and a chemical player, a new fluxing agent has been developed: the InnRoad Protect (IRP). This new fluxing agent show a similar mechanism as the mineral fluxing agent as it evaporates in the air after laying and thus, can be identified as "volatile fluxing agent". For obvious reasons, the comparison of performances is only made between mineral fluxing agents and this new fluxing agent. These latest shows unique evaporation properties (Figure 1), thanks to a very tight boiling range (according to the ASTM D86). It allows the binder to recover faster its original properties for surface dressing and to improve the cohesion build-up for storable mixes, cold mixes and even microsurfacing, leading to a better durability: the pavement is less sensitive at the young age.

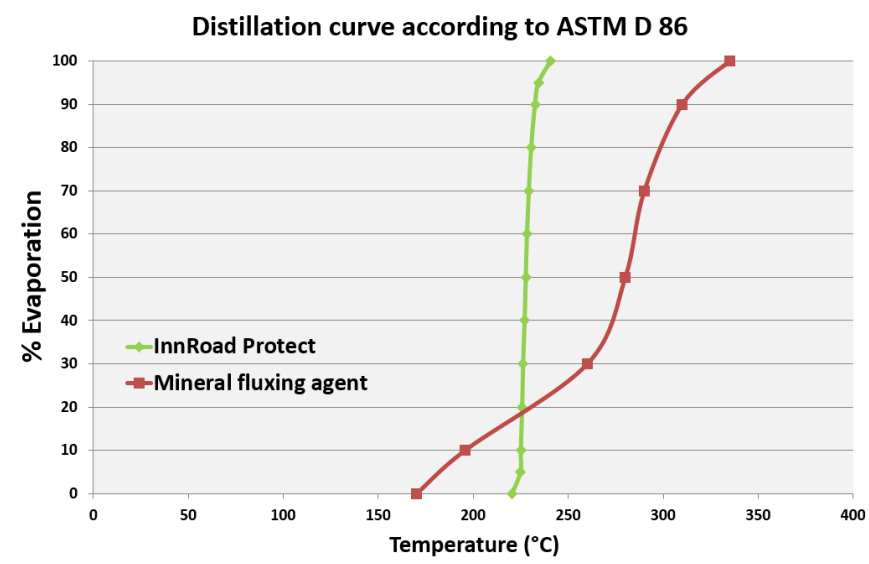

Figure 1: Distillation curves of the new fluxing agent and a mineral fluxing agent according to ASTM D 86

Fluxing agents are also characterized by their "fluxing power": their ability to decrease the viscosity of bitumen, with a content as low as possible. The table 1 highlights the fact that a decrease of around 20% of flux oil can be done for surface dressing with fluxed bitumen for example.
Thus, the new fluxing agent, characterized by its intrinsic properties, is more efficient, and added-values can be seen in a broad type of applications.

Table 1. Indicative performances of pseudo viscosity STV (10mm@40°C)

	Mineral Fluxing agent STV (s)	InnRoad Protect STV (s)
70/100 Bitumen + 4.0%	> 1200	1000
70/100 Bitumen + 4.5%	1000	680
70/100 Bitumen + 5.0%	900	480
70/100 Bitumen + 6.0%	650	380

Another aspect, carefully observed by the users is the HSE (Health, Safety and Environment) profile of every new flux oil used in this industry. After many years of using cut-back bitumen and CMR (carcinogenic mutagenic toxic reproduction) flux oil (those additives would be classified as H350 or H351 i.e, with a carcinogen ranking of 1A / 1B, according to the regulation (EC) No 1272/2008 on Classification, Labelling and Packaging of Substances and Mixtures, commonly known as CLP Regulation**[3]** entered into force on 20th January 2009), the road manufacturing industry took significant recommendations**[4]** to put aside those type of products and recommend the use of non-classified products or labelled fluxing agents, as long as they're not CMR.
As mentioned before, there is only 2 families in the market and regarding the labelling, there is no doubt that biosourced methyl esters have an excellent HSE profile owing to the fact that they do not show any classification (labelling or hazards sentences). On the opposite, mineral flux oils show a poor HSE profile, with several classifications (Table 2).
The 1st REACH registration tests of InnRoad Protect allowed to show the absence of hazards towards the environmental and health profile, which would enable to decrease the pressure undergone by the road industry regarding the use of volatile fluxing agents. This is strengthened by a higher flash point which lower the ATEX zone. To be noted that vegetal flux oils show a higher flash point, because these products are not volatile.

Table 2. Characteristics of fluxing agents on the market

HSE Profile	Mineral fluxing agent	Vegetal flux oil	InnRoad Protect
Health profile*	Labelling H304[1] and / or H335[2], H336[3] 	Not classified as dangerous	Not classified as dangerous
Environmental profile*	Potentially persistent	Non persistent	Non persistent

	Labelling H411[4] or H412[5] 	No labelling	No labelling
Flash point Pensky-Martens	Low (< 90°C) : could lead to ATEX zone (Explosive atmosphere)	High (> 160°C)	Medium: > 114°C

*Data obtained on the MSDS of each product, according to CLP Regulation
[1] May be fatal if swallowed and enters airways
[2] May cause respiratory irritation.
[3] May cause drowsiness or dizziness.
[4] Toxic to aquatic life with long lasting effects.
[5] Harmful to aquatic life with long lasting effects.

Table 3. Indicative performances of Flash point (Fp) Pensky-Martens

	Mineral Fluxing agent Fp (°C)	**InnRoad Protect Fp (°C)**
70/100 Bitumen + 19%	93	117

3. LIFE CYCLE INVENTORY (LCI) ANALYSIS

In addition of the toxicity and ecotoxicity evaluations, a Life-Cycle Assessment (LCA) procedure was performed with the software Simapro 8.5, in conformity with the ISO 14040 and ISO14044 standards using publicly-available and Solvay-specific scientific data*. This allows to create an inventory of all the environmental impacts of the new fluxing agent (resource consumption, emissions to soil, air and water, figure 2) including human toxicity in a 'cradle-to-gate' approach**, from raw material extraction to production until it leaves the plant (without packaging) **[5].** A LCA helps to confirm and ascertain the environmental benefits of a single product compared to competing products in the market. These benefits could come from better technical performance, lower energy consumption or lower pollutant emissions during the use phase. This first comparison is based on the Global Warming Potential (GWP) of a typical mineral fluxing agent and the new fluxing agent available on the market. The GWP allows comparisons of the global warming impacts of greenhouse gases emissions during the production and life of the products considered, and expressed in CO2-equivalent for One ton of product. The larger the GWP, the more that a given gas warms the Earth compared to CO_2 over that time period. The time period usually used for GWPs is 100 years. GWPs provide a common unit of measure, which allows analysts to add up emissions estimates of different gases (e.g., to compile a national GreenHouse Gases (GHG) inventory), and allows policymakers to compare emissions reduction opportunities across sectors.

** The data sources are:*

- *Site data have been collected for the year 2019 according to the Solvay standard template,*
- *For operations not related to the site and for raw materials, Ecoinvent 3.4 data have been used*
- *For the existing competitor product, a range of proxies in existing Ecoinvent database has been used.*
- *For the energy sourcing, we have considered the electricity production in the relevant country (module EcoInvent FR)*
- *The transport of main material to the site has been evaluated in this study.*

***due to lack of data regarding the whole life of fluxing agents (application phase, lifespan and end of life), it was not possible to perform a cradle-to-cradle approach*

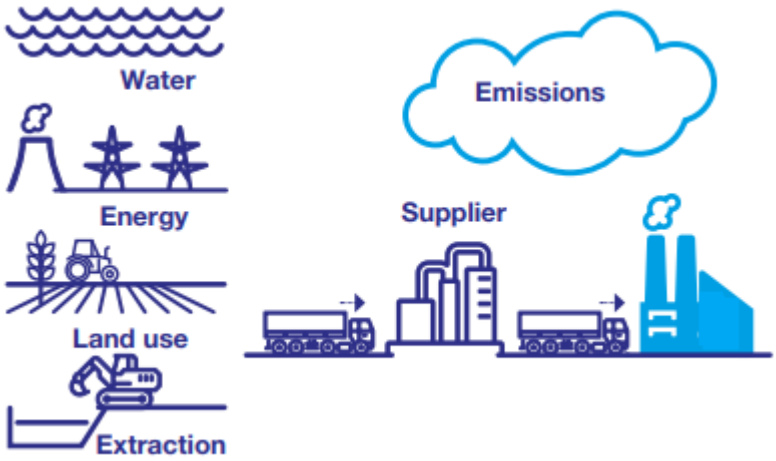

Figure 2: Environmental impact during the manufacture of a product

The new fluxing agent is obtained from the reaction of a by-product (and thus avoid the incineration of waste) with a plant-derived compound. The vegetal bio sourced part allows us to count it as biogenic carbon sequestration in the product, which has a positive effect of the environmental footprint of the product. Indeed, this biogenic carbon is considered as "carbon neutral" along his life cycle, i.e. at the end of life, the CO_2 release from this product is equivalent to the carbon capture in the production of bio-based raw material.
Despite a large uncertainty on the proxy (similar data obtained in EcoInvent) for mineral fluxing agent (assimilated to a mixture of generic petroleum distillates), the resulting GWP of the new generation of flux oil is significantly lower than the GWP of usual mineral fluxing agents (Table 4), thanks to the biogenic content. Indeed, producing a ton of InnRoad Protect generates at least 40% less emissions of CO_2 compared to the manufacture of one ton of mineral fluxing agent.

Table 4. GWP of fluxes (for 1 kg of product)

Impact category	Unit	InnRoad Protect	Mineral Fluxing agent (proxy)
GWP 100y	Kg CO_2 eq	1.29	0.90
Biogenic content	Kg CO_2 eq	- 0.78	
Resulting GWP	**Kg CO_2 eq**	**0.51**	**0.90**

Another aspect to consider is the use of fluxing agents when making roads, which can be decomposed in two parts: the application / use of fluxed bitumen / fluxed emulsions and the life span of the road itself.

In this analysis, only the dosage of fluxing agent has been taken into account. Indeed, the heating of the binder (during the application or during the manufacture of the emulsion) generates VOC emissions but those emissions are not a contribution substance to the GWP indicator. They have an impact on the respiration effects on human health and photochemical oxidation but a better knowledge of the emission rate of these substances during the application phase is required to perform an assessment of the impact on human health during this life cycle phase, and a priori, there is no additional CO_2 emission during this phase. Moreover, it has been estimated that infrastructure (equipment, etc …) and transport of products are equivalent whatever the flux and no consolidated data are available to evaluate precisely the lifespan of the road. Thus, none of these parameters have been included in the comparative assessment. The following example considers a fluxed modified bitumen, containing 5.4% of mineral fluxing agent or 4.2% of InnRoad Protect, to obtain the same technical performances. Thus, in term of CO_2 emissions on all life cycle, a fluxed bitumen, containing the new fluxing agent, presents a footprint (Figure 3) of 2.2 kg / ton bitumen, compared to 4.9 kg CO_2 / ton bitumen for the mineral fluxing agent, thanks to its vegetal bio-sourced part which captured CO_2. The potential saving of using the new fluxing agent is ~2.7 kg CO_2 / ton bitumen in this type of application, which can be pointed out for environmental aspect when answering to tender.

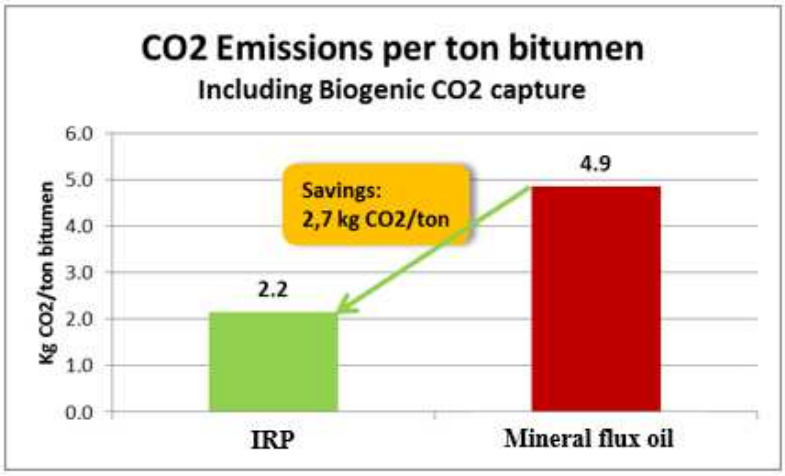

Figure 3: CO_2 emission per ton of fluxed bitumen used

4. TECHNICAL BENEFITS IN SURFACE DRESSING EMULSIONS

Surface dressing is one of the most popular road maintenance technic in some countries, as it is a cost effective technic to maintain a good level of secondary road networks. Binders are spread on top of the road and to do that, fluxing agents are the key additives to enable that laying. The new fluxing agent has been designed to comply with the specifications required by the 2 type of binders which are generally used: anhydrous fluxed bitumen and bitumen emulsions, which have a predominant market share. In this article, only bitumen emulsions results are displayed and discussed.

In bitumen emulsions, flux oils play a significant role in making easier the emulsification process (especially for high viscosity binders). Moreover, after laying on the road, fluxing agents improve the coalescence of the binder's droplets in the emulsion hence accelerating the curing process of the emulsion. Two highly modified (cohesion > 1.2 J/cm²) bitumen emulsions have been manufactured and characterized (Table 5). In the first emulsion, high amount of mineral flux oil (>3%) has been used in the binder to be in accordance with the EN 13808 specifications. On the contrary, with IRP, the amount of flux oil has been drastically reduced (-25%) with no negative influence on the emulsion properties.

Table 5. PmB emulsions properties depending on flux oil type

Emulsion type		**C69/70 BPF 2**	**C69/70 BP 2**
Flux oil type		Mineral flux oil (MF)	InnRoad Protect
Flux oil content in emulsion	%	> 3	< 3
Binder content : NF EN 16849			
Binder content	%	70.2	69.4
Efflux time : NF EN 12846-1			
4 mm at 40°C	s	12	17
2 mm at 40°C	s	140	200
Residue on sieving : NF EN 1429			
0,500 mm sieve	%	0.02	0.05
0,160 mm sieve	%	0.27	0.24
Droplet size distribution - Laser diffraction			
Mean diameter	µm	3.50	2.91
Standard deviation	/	0.41	0.38
Breaking value : NF EN 13075-1			
Breaking value (Forshammer)	/	49	44
Adhesivity : NF EN 13614			
Diorite	%	≥75	≥75
Quartzite	%	≥75	≥75

The new flux oil allows getting improvement in viscosity of the emulsion, droplet size distribution and breaking value compared to mineral flux oil.
The two emulsions have been stabilized according to EN 13074-1&2 standard and the stabilized binders have been characterized to evaluate the stiffness recovery. Table 6 shows the significant difference in the penetration and Ring & Ball (R&B) temperature values between the two binders. These results confirm that IRP is much more effective in the stiffness recovery of the binders. As expected, the maximum cohesion values are similar between the two binders, because the cohesion is mainly brought by the polymer content in the binder. However the maximum cohesion temperature is slightly shifted to upper values. Thanks to some polar affinities with water, IRP might diffuse to water, explaining good efficiency in the recovery of initial properties of the binders. Some works have been initiated to better understand this potential complementary mechanism.

Table 6. Properties of the residual binders after stabilization (NF EN 13074-1&2)

Emulsion type	**C69/70 BPF 2**	**C69/70 BP 2**	**NF EN 13808 specifications**
Flux oil type	MF	IRP	
Flux oil content in emulsion (%)	> 3	< 3	
Penetration 25°C (1/10 mm) NF EN 1426	55	40	≤ 100
Ring & Ball temperature (°C) NF EN 1427	58.2	61.0	≥ 50
Cohesion (J/cm²) NF EN 13588	1.27	1.24	≥ 1.2
Temperature max cohesion (°C)	40	45	/

Many field trials have already been done during 2018 and 2019 with very promising technical results, confirming the versatility and high efficiency of this innovation. A CIRR**[6]** surface dressing emulsion'jobsite done in july 2019 confirmed the previous observations about the laying and the early technical performances.The new flux oil has been shown to significantly improve the coalescence of bitumen droplets on job site by decreasing the breaking time of the emulsion hence leading to a shorter time for stiffness recovery of the binder at the early stage of the job site.

5. ASPHALT WITH IMPROVED WORKABILITY AND STORABLE ASPHALT

Since the beginning of 2000's, the development of WMA, Warm mix Asphalt, allowed the road companies to meet expectations regarding sustainable development by lowering the production and laying temperatures of asphalt. However, with these technologies, workability has to be preserved especially for manual laying where workability may be an issue. Flux oils have the potential to be used in small concentrations in bitumen in order to prepare hot or warm mix asphalt with improved workability. Vegetal flux oils (Fv) are generally preferred because their flash point allows them to be used in such applications. Mineral flux oils, on the contrary, show good technical performances but are not used because of their too low flash point compared to the manufacture and laying temperatures.
The new flux oil has been investigated in asphalt formulations to evaluate its behaviour regarding improvement of workability for manual laying. Workability is linked in some extent to the evolution in dynamic viscosity of the binder with a decrease in the temperature. Binders have been investigated with dynamic viscosity, penetration and R&B temperature measurements.
Figure 4 shows that either 3% of vegetal flux oil (Fv) or 2% of IRP are necessary to reduce the dynamic viscosity of the binder in the 100-120°C temperature window which is relevant to temperatures measured during manual laying of asphalt.

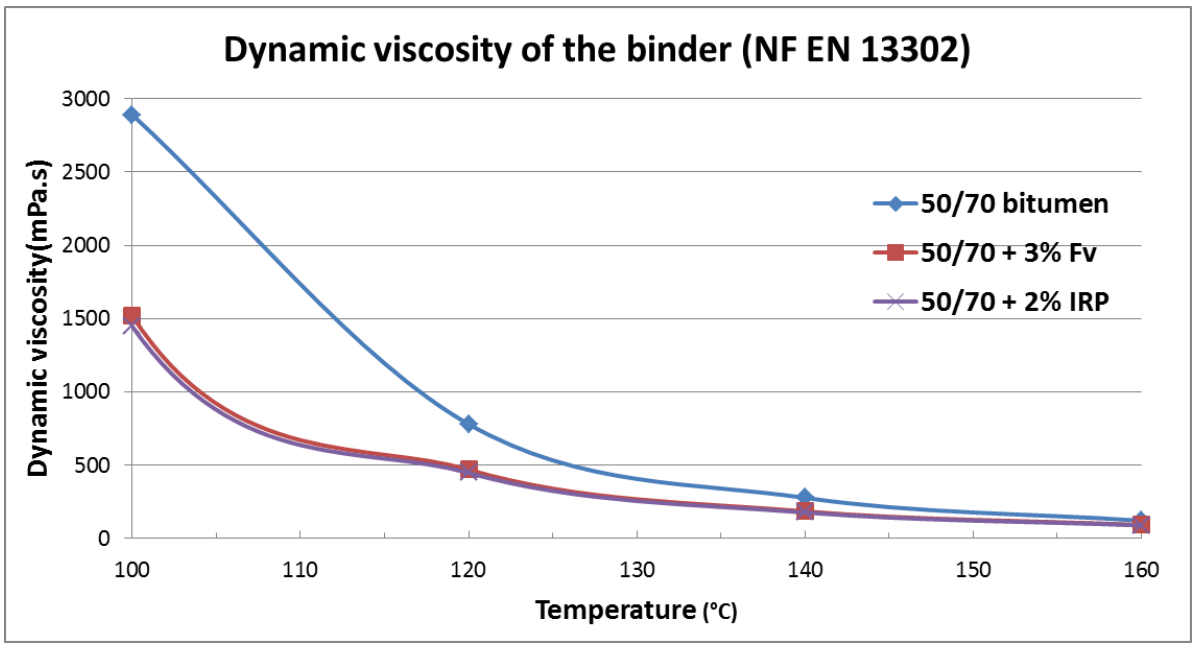

Figure 4: Dynamic viscosity of the binders

The properties of the fluxed bitumen have been compared with those of a 50/70 pen grade bitumen either before or after stabilisation (NF EN 13074-1&2 standards).

Table 7. Properties of the residual binders after stabilization (NF EN 13074-1&2)

Sample		50/70 bitumen	50/70 + 3% Fv	50/70 + 2% IRP
Penetration at 25°C, 1/10mm	NF EN 1426	55	168	157
Ring & Ball temperature, °C	NF EN 1427	47,0	42.0	43.0
Properties after stabilisation NF EN 13074 1&2				
Penetration at 25°C, 1/10mm	NF EN 1426	/	94	52
Ring & Ball temperature, °C	NF EN 1427	/	45.8	50.0

Results show that vegetal flux oil and IRP are effective in changing the grade of a bitumen from a 50/70 to a softer grade bitumen (close to a 160/220 grade). However the main differences are observed after stabilisation. Indeed, while the fluxed bitumen using vegetal flux oil remains very soft, the one formulated with IRP shows the same properties than the neat 50/70 grade bitumen. Consequently, IRP allows a much more significant cohesion build-up of the binder compared to vegetal flux oil.

In order to evaluate the benefits of flux oils on workability, three 0/6 asphalt mixes have been manufactured with 0/2 from Aubron quarry, 0/4 from Saremer quarry and 2/6 from Aubron quarry. The binder content is 6% of the composition and three different binders have been used in this study:

-50/70 pen grade bitumen → Asphalt 50/70
-50/70 fluxed with 3% of vegetal flux oil → Asphalt 50/70 + 3% Fv
-50/70 fluxed with 2% of IRP → Asphalt 50/70 + 2% IRP

The three asphalt mixes have been manufactured at 140°C.

The Nynas workability device test has been shown to be relevant for measuring workability of asphalt mixes depending on temperature, density, binder formulation, … **[7][8][9]**

In this study, the three asphalt mixes described above have been analysed with Nynas workability device test at different temperatures and at constant density. The curves displayed in Figure 5 highlight the effective impact of flux oils on workability of the asphalt mixes depending on the temperature. Asphalt mix formulated with IRP shows similar behaviour than asphalt mix formulated with vegetal flux oil and both of these formulations show better workability compared to the asphalt mix reference (without flux oil).

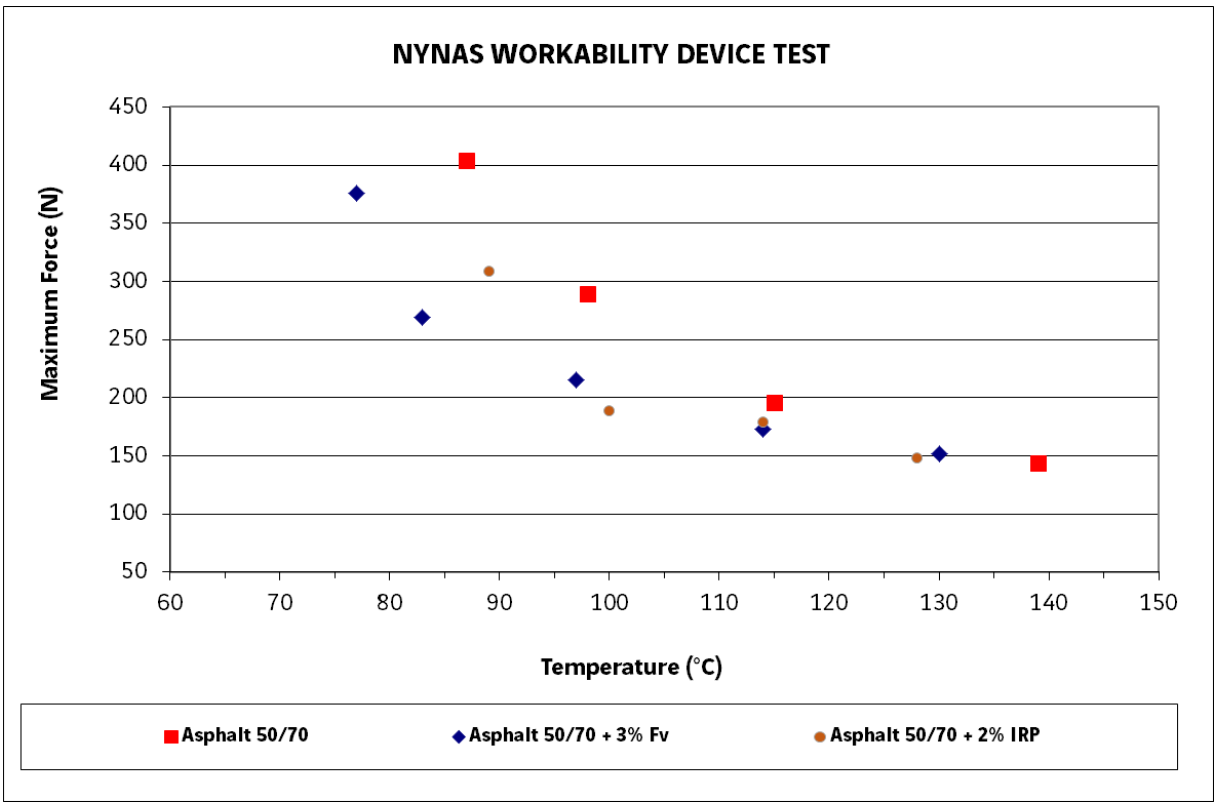

Figure 5: Nynas workability device test of the asphalt mixes at different temperatures

The gyratory shear compactor test and mechanical tests such as IT-CY and Duriez tests have been performed in order to compare the behaviour during compaction of the three asphalt mixes and then cohesion build-up behaviour of the two asphalt mixes formulated with flux oils. Results displayed in Table 8 show that IRP is much more effective than vegetal flux oil in order to obtain asphalt mixes with good mechanical properties.

Table 8. Mechanical performances of the asphalt mixes

Asphalt sample		50/70 bitumen	50/70 + 3% Fv	50/70 + 2% IRP
Gyratory compaction Voids at 60 gyrations (%)	NF EN 12697-31	5,1	5,5	4,7
Stiffness Modulus IT-CY, 10°C, 124ms (MPa)	NF EN 12697-26	/	2900	5400
Compression resistance at 18°C R (MPa)	NF P 98-251-4	/	4,96	6,74

Studies on storable asphalt mixes have also been performed in laboratory and then validated industrially by the manufacture of more than 1000 tons of storable mixes. For storable mixes, the amount of flux oil has been significantly increased to a concentration of around 17% in the bitumen. The very low dynamic viscosity of the fluxed bitumen allowed a production of the storable mix at 110°C which is a temperature below the flash point of the highly fluxed bitumen (~117°C). The feedback from the field is excellent with suitable storable behaviour and good cohesion build-up once applied as a road maintenance technique.

6. CONCLUSION

The challenge of sustainability is answered every day by the road construction thanks to a focus on the recycling, the limitation of asphalt manufacturing temperatures and the selection of more sustainable additives which was not possible for the fluxing agent additives until now. Indeed, road contractors had to choose between technical performances or HSE' profile. Since 3 years, a new fluxing has been developed and Figure 6 allows to have a full picture of the 3 type of fluxing agents available on the market now: it shows that the new fluxing agent combines the best of the two previous flux oil family with a high level of technical performances and absence of classification for

both the human being and the environment. On top of being biodegradable, InnRoad Protect generates 40% less CO_2 emissions than mineral fluxing agent.
In-situ tests have been carried out since 2018 on several maintenance road applications and global technical feedback regarding the laying and roads'behavior after several months show the versatility of this new generation of fluxing agent.

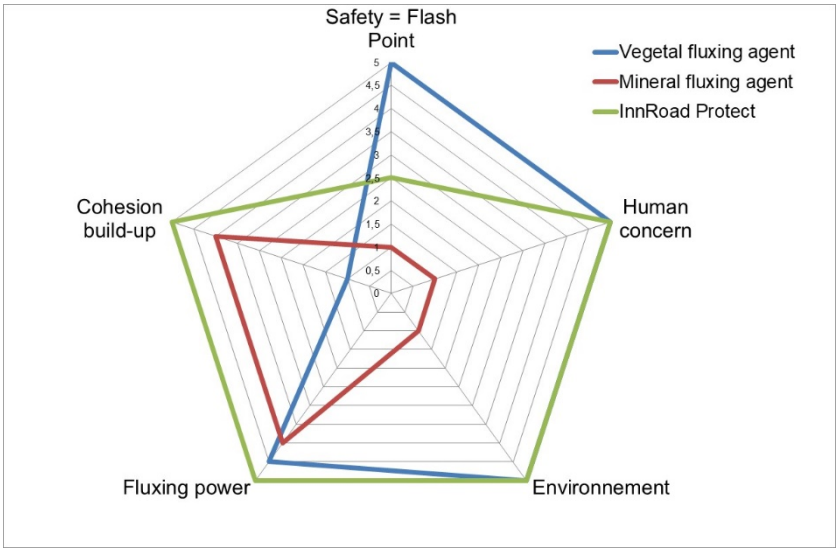

Figure 6: Comparison of the 3 type of fluxing agents according to their technical performances and HSE profile

REFERENCES

[1] Alfos C., David K., Marcilloux J., Formulation of solvents for bitumen based on vegetable oil methyl esters, OCL-Oléagineux Corps Gras Lipides, 12, 2005, pp. 392-399
[2] Antoine J-P., Marcilloux J., Anhydrous binder for mixes or surface dressing road goes to green, OCL-Oléagineux Corps Gras Lipides, 12, 2005, pp. 304-307
[3] Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures
[4] Usirf (2005), Impacts sanitaires des fluxants, fluidifiants et produits anti-kérosène, groupe de travail Administration/Usirf, mars 2005.
[5] A. Wathelet, Environmental footprint of InnRoad Protect and comparison with Mineral Fluxing agent, Solvay confidential internal publication, 2019,
[6] CIRR Comité Innovation Routes et Rues by IDRRIM : The Institute of Roads, Streets and Infrastructures for Mobility
[7] Brion Y., Le Roux C., Linder R., Moonen R., Mesure de l'évolution de la cohesion à l'émulsion au jeune âge par le maniabilimètre Nynas, Revue Générale des Routes et de l'Aménagement, n° 769, 1999, pp. 56-61
[8] Fabre des Essats A., Dony A., Roux J-N., Gaudefroy V., Influence de la compacité des corps d'épreuves sur l'évaluation en laboratoire de la maniabilité des enrobés tièdes, Revue Générale des Routes et de l'Aménagement, n°928, 2015, pp. 56-59
[9] Fabre des Essarts A., Dony A., Faucon-Dumont S., Gaudefroy V., Roux J-N., Evaluation of tools for measuring the workability of bituminous asphalts, E&E Congress 2016, 6th Eurasphalt & Eurobitumen Congress, 2016, Praha Czech Republic