

## Thiencarbazone-methyl (TCM) and Cyprosulfamide (CSA) – a new herbicide and a new safener for use in corn

*Thiencarbazone-methyl (TCM) und Cyprosulfamide (CSA) – ein neues Herbizid und ein neuer Safener zur Anwendung in Mais*

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### Summary

Thiencarbazone-methyl is a new herbicide for the selective control of grasses and broadleaf weeds primarily in corn. The active ingredient belongs to the chemical class of sulfonyl-amino-carbonyl-triazolinones (SACT) and acts as an inhibitor of the ALS-enzyme. The compound offers cross spectrum activity against grasses and broadleaf weeds and can be applied at the pre-emergence and the post-emergence timing. The use rate depends on the application timing and may vary from 22 – 45 g a.i./ha in pre-emergence applications and 10 – 15 g a.i./ha in post-emergence applications. Sequential treatments are possible as long as the maximum seasonal dose of 45 g a.i./ha is not exceeded. In commercial corn herbicides, TCM is always combined with safener technology such as the novel safener cyprosulfamide and with other herbicidal active ingredients. In pre-emergence applications, the primary herbicidal mixpartner is isoxaflutole. In herbicides designed for post-emergence use, TCM is co-formulated with foramsulfuron, iodosulfuron or tembotrione. The commercial herbicides composed of TCM and CSA plus sulfonylurea or triketone partners have demonstrated high weed control success in conventional and herbicide-tolerant corn production systems. Depending on the product, the potential for one pass weed control has been confirmed. Control of perennial grasses like *Sorghum halapense* and *Elymus repens* together with control of problem weeds like *Polygonum convolvulus* and suppression of *Cirsium arvense* and *Convolvulus arvensis* appear to be among the most attractive features of TCM-based herbicides under European conditions. High crop tolerance of herbicides combining two or three highly active ingredients in one commercial product is ensured by the novel safener cyprosulfamide which can protect corn via root uptake and via leaf uptake from herbicide damage.

**Keywords:** Herbicide, pre-emergence, post-emergence, residual activity, sulfonylaminocarbonyl-triazolinone, weed control

### Zusammenfassung

Thiencarbazone-methyl ist ein neues Herbizid zur selektiven Bekämpfung von Ungräsern und dikotylen Unkräutern vor allem in Mais. Der Wirkstoff gehört zur Klasse der Sulfonylaminocarbonyltriaolinone (SACT) und wirkt als ALS-Hemmer. Der Wirkstoff besitzt ein breites Wirkungsspektrum und kann im Voraufbau oder im Nachaufbau angewandt werden. Die empfohlene Dosis hängt vom Anwendungszeitpunkt ab und liegt zwischen 22 – 45 g a.i./ha im Voraufbau und bei 10 – 15 g a.i./ha in Nachaufbau. Spritzfolgen sind möglich, solange die Maximaldosis von 45 g a.i./ha nicht überschritten wird. In kommerziellen Maisherbiziden wird TCM immer mit einem Safener, meist mit Cyprosulfamide, und weiteren herbiziden Wirkstoffen kombiniert. Für Voraufbauanwendungen ist Isoxaflutole der primäre Mischpartner. In Nachaufbauherbiziden wird TCM gemeinsam mit Foramsulfuron, Iodosulfuron oder Tembotrione formuliert. Die Herbizidkombinationen aus TCM + CSA und Sulfonylharnstoff- oder Triketonpartner haben ihren Nutzen für die Unkrautbekämpfung in konventionellen und herbizid-toleranten Maisproduktionssystemen unter Beweis gestellt. Eine einmalige Anwendung der am breitesten wirkenden Produkte kann die Unkrautbekämpfung für eine gesamte Anbausaison sichern. Besonderen Wert der TCM-haltigen Produkte hat die Wirkung gegen perennierende Gräser wie *Sorghum halapense* und *Elymus repens*, die gekoppelt ist mit der Bekämpfung des Problemunkrauts *Polygonum convolvulus* und der unterdrückenden Wirkung gegen *Cirsium arvense* und *Convolvulus arvensis* unter europäischen Bedingungen. Die sichere Verträglichkeit der Kombiherbizide, die zwei oder drei herbizide Wirkstoffe enthalten, wird durch den neuen Safener Cyprosulfamide gewährleistet, der den Mais nach der Aufnahme durch Wurzeln und Blätter vor Herbizidschäden schützt.

**Stichwörter:** Dauerwirkung, Herbizid, Nachaufbau, Sulfonylaminocarbonyltriaolinone, Unkrautbekämpfung, Voraufbau

## 1. Introduction

Chemical weed control in maize with selective herbicides has long been dominated by triazines for broadleaf weed control and amides for grass control. Later, important additions to the herbicide portfolio available to the corn producer included, among others, triketones and sulfonylureas. The sulfonylureas opened the opportunity to consistently control emerged annual and perennial grasses and various broadleaf species in the established crop but were lacking soil residual activity. Sulfonyl-amino-carbonyl-triazolinones (SACT) offer immediate and residual cross spectrum control of grasses and broadleaves and are active against a large variety of emerging and established mono- and dicotyledonous weeds (MUELLER et al., 2011).

All three commercial herbicides belonging to the chemical class of sulfonyl-amino-carbonyl-triazolinones act as inhibitors of the aceto-lactate-synthase (ALS) enzyme. The first generation of the SACTs is represented by the wheat herbicides propoxycarbazone-sodium (ATTRIBUT<sup>®</sup>, OLYMPUS<sup>®</sup>; FEUCHT et al., 1999) and flucarbazone-sodium (EVEREST<sup>®</sup>; SANTEL et al., 1999). Both active ingredients selectively control grasses and broadleaf weeds after postemergence application. The second generation SACT herbicide thien carbazole-methyl offers a more diverse utility for weed control. It can be used pre-emergent and post-emergent, and in combination with proper safener technology it can be applied to wheat and corn. Thien carbazole-methyl (TCM) obtained its first registration 2008 in Romania and is now being registered in important corn producing countries of Europe and other parts of the world. In corn herbicides, TCM is safened by the recently developed safener cyprosulfamide. Trade names of various mixtures containing TCM and CSA together with other corn herbicides include Adengo<sup>®</sup>, Corvus<sup>®</sup>, Capreno<sup>®</sup> and Maister power<sup>®</sup> for selective use in maize.

## 2. Materials and methods

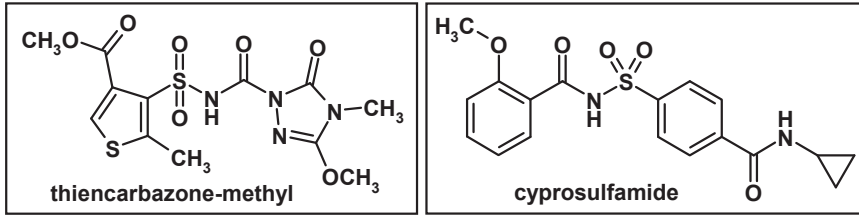
Replicated small plot field trials were laid out in randomized block design with three replications per treatment. They were conducted in commercial maize fields with natural weed infestations in most of the important corn growing areas of Europe and North America. Formulated herbicides were applied with a knapsack sprayer in 200 l/ha water. Weed control and crop tolerance were rated as % effect on a 1 - 100 scale by visual assessments in comparison with untreated control plots.

Formulated commercial products were used in the field experiments and included Merlin<sup>®</sup> 480 SC (isoxaflutole), Adengo<sup>®</sup> 465 SC (isoxaflutole + TCM + CSA), Maister<sup>®</sup> 61 OD (foramsulfuron + iodosulfuron + isoxadifen) and Maister power<sup>®</sup> 58 OD (TCM + foramsulfuron + iodosulfuron + CSA). For applications of TCM + CSA, a suspension concentrate TCM + CSA 450 SC was used. The formulated products were diluted with water before spraying. When applications of TCM + CSA were made post-emergent between the 2 and 6 leaf stage of maize, 1 l/ha of a formulated methylated rape seed oil (Mero<sup>®</sup>) was added to the aqueous spray solution to ensure best uptake of the safener and the herbicidal active ingredients.

## 3. Results and discussion

### 3.1 Thien carbazole-methyl (TCM) and Cyprosulfamide (CSA) chemistry

Thien carbazole-methyl (PHILBROOK and SANTEL, 2007) marks the latest progress in SACT herbicide technology (Fig. 1). In the novel molecule two ring systems, a double substituted thienyl moiety and a methyl and methoxy substituted triazolinone system, are connected with each other by a sulfonamide bridge. In general, the SACT-molecule structure follows the principles of classical sulfonylureas. However, the "sulfonylurea bridge" that connects the two ring systems is one element shorter than in sulfonylureas. The urea bridge and the triazolinone ring share one nitrogen atom.



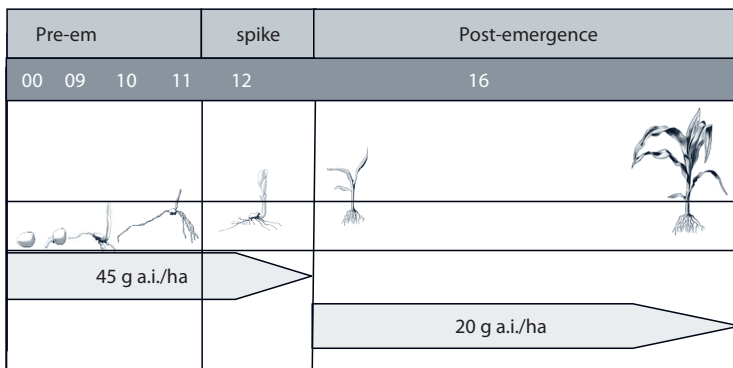
**Fig. 1** Structural formulas of thien carbazole-methyl and cyprosulfamide.

**Abb. 1** Strukturformel von Thien carbazole-Methyl und Cyprosulfamide.

Structural similarities between TCM and sulfonyleureas thus exist but the active ingredients also share the same molecular mode of action and act as powerful inhibitors of the acetolactate-synthase (ALS). Cyprosulfamide (Fig. 1) is a novel safener that protects corn from herbicide damage and belongs to the chemical class of aromatic sulfonamides. CSA was co-developed with TCM. The safener reliably protects corn from damage after soil application and after foliar application of TCM through induction of enhanced herbicide metabolism via gene activation. The herbicidal activity is maintained in the presence of the safener.

### 3.2 Application timings and use rates

Generally, TCM can be applied pre-emergent or post-emergent up to the six leaf stage of maize (Fig. 2). The registered maximum use rate for a single application is 45 g a.i./ha. This dose can be applied from the time of seeding of the crop to the full development of the second leaf of maize. After maize has reached the two leaf stage, a maximum use rate 20 g a.i./ha is registered and treatments have to be completed when the sixth leaf on maize has fully unfolded (crop stage 16). Treatments of TCM containing herbicides may be split. Commercial products based on TCM are designed accordingly, allowing single applications or sequential applications at useful doses.



**Fig. 2** Crop development stages, application timings and maximum use rates of TCM in maize.

**Abb. 2** Entwicklungsstadien, Anwendungszeitpunkte und maximale Aufwandmengen von TCM.

The maximum seasonal dose of CSA is 154 g a.i./ha. It can be applied any time between seeding of the crop and development of its sixth leaf.

### 3.3 Weed control and crop tolerance

During the main development period (2004-2008) of TCM numerous field trials have been carried out with the objective to identify its use potential. Weed control data obtained clearly show that TCM is a cross spectrum herbicide (Tab. 1). Since it provides control of a large variety of grasses and broadleaf weeds and offers strong suppression of difficult to control species like *Sorghum halapense* and

others. With its wide weed control spectrum TCM is an excellent new component to be added to established herbicides to form new broad spectrum commercial products for selective weed control in maize.

**Tab. 1** Range of weed control of thien-carbazone-methyl at different use timings.

**Tab. 1** Die Wirkungsbreite von Thien-carbazone-methyl zu unterschiedlichen Anwendungszeitpunkten.

Efficacy range	Use rate and timing of herbicide application	
	40 g TCM/ha; pre-emergence	15 g TCM/ha; post-emergence
80 – 94 % control	20 weed species	39 weed species
95 – 100 % control	47 weed species	53 weed species

The strong herbicidal activity of TCM + CSA observed when applied pre-emergent to early post-emergent allowed the creation of a new commercial product, in which the 4-HPPD inhibitor isoxaflutole and the ALS inhibitor TCM are combined together with the safener CSA in a 465 SC formulation (SANTEL and PHILBROOK, 2008). In this new product, sold under the trade names ADENGO<sup>®</sup> and CORVUS<sup>®</sup>, both active ingredients complement each other and offer more complete commercial weed control compared to the individual components (Tab. 2).

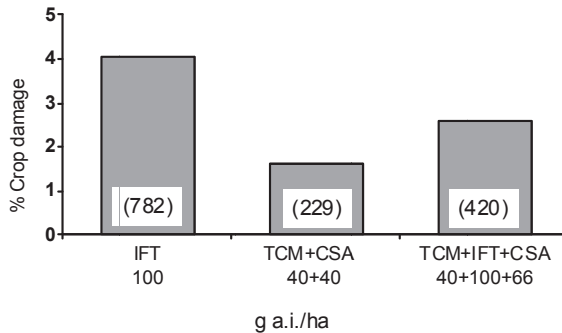
**Tab. 2** Efficacy of different herbicide treatments against important maize weeds after application at the pre-emergence to early post-emergence (max. 2 leaf stage of maize) stage of the crop. (n) = number of trials.

**Tab. 2** Die Wirkung verschiedener Herbizidanwendungen gegen wichtige Maisunkräuter nach Anwendung im Vorauf- oder frühen Nachauf- (max. 2-Blattstadium des Mais) der Kultur. (n)=Anzahl Versuche.

Weed species	Herbicide treatments		
	Isoxaflutole 100 g a.i./ha	TCM + CSA 40 + 40 g a.i./ha	IFT + TCM + CSA 100 + 40 + 66 g a.i./ha
% Control of monocotyledonous weed species			
<i>Agropyron repens</i>	49 (36)	-	76 (32)
<i>Avena fatua</i>	68 (10)	94 (1)	98 (9)
<i>Digitaria sanguinalis</i>	84 (115)	79 (24)	90 (29)
<i>Echinochloa crus-galli</i>	83 (328)	91 (41)	92 (148)
<i>Panicum mileaceum</i>	84 (27)	91 (7)	91 (6)
<i>Pennisetum glauca</i>	83 (14)	86 (2)	91 (9)
<i>Setaria verticillata</i>	82 (36)	82 (11)	95 (7)
<i>Setaria viridis</i>	82 (111)	91 (17)	96 (36)
<i>Sorghum halapense</i>	73 (24)	73 (1)	80 (6)
% Control of dicotyledonous weed species			
<i>Abutilon theophrastii</i>	95 (69)	89 (12)	91 (10)
<i>Amaranthus retroflexus</i>	91 (210)	100 (13)	95 (80)
<i>Chenopodium album</i>	92 (491)	89 (53)	96 (223)
<i>Cirsium arvense</i>	67 (18)	-	78 (17)
<i>Equisetum arvense</i>	43 (7)	-	78 (6)
<i>Matricia inodora</i>	94 (9)	100 (3)	100 (10)
<i>Mercurialis annua</i>	54 (61)	59 (16)	91 (13)
<i>Polygonum aviculare</i>	49 (68)	85 (14)	98 (27)
<i>Polygonum convolvulus</i>	40 (167)	85 (29)	87 (105)
<i>Polygonum persicaria</i>	84 (122)	100 (12)	99 (47)
<i>Solanum nigrum</i>	96 (243)	91 (33)	98 (79)
<i>Stellaria media</i>	90 (75)	97 (8)	99 (34)
<i>Viola arvensis</i>	79 (50)	97 (4)	92 (48)
<i>Xanthium strumarium</i>	70 (14)	85 (2)	86 (10)

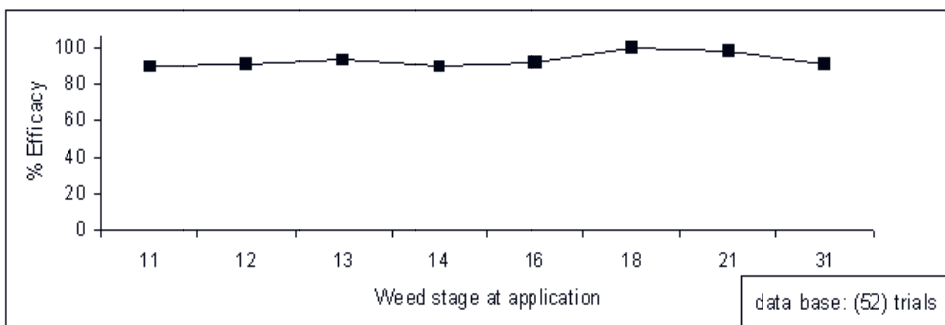
The crop tolerance of the commercial mixture of IFT + TCM + CSA is maintained by the safener CSA and appears favorable (Fig. 3). The overall crop reaction with an average 2.6 % response rating over 420 trials indicates very high crop safety. In comparison with isoxaflutole, the selectivity of the new herbicide mixture is improved by the safener.

The addition of TCM to any herbicide for pre-emergence or post-emergence use results in an expansion of the weed control spectrum. A particular value of the TCM addition to foramsulfuron + iodosulfuron (Maister®) to form Maister power® is the inclusion of *Polygonum convolvulus* into the spectrum of susceptible weeds (Fig. 4). Many corn herbicides miss this problem weed and therefore a mid to late post-emergence treatment with a dicamba- or bromoxynil-containing product needs to be used to control this weed species. TCM, which delivered on average 85 % control after pre-emergent application, offered even better control when used in combination with foramsulfuron and iodosulfuron in post-emergence. Sensitive development stages of *Polygonum convolvulus* then ranged from the one true leaf stage (11) to the stage of stem elongation (31) and possibly beyond (Fig. 4). Besides the expansion of the weed control spectrum, TCM, when combined with foliar herbicides, also adds residual control that extends the time during which weed control can be achieved. Against *Chenopodium album*, the period of control could be extended by 5 - 6 weeks in 2 model trials when compared to the TCM free comparison mixture (Fig. 5).



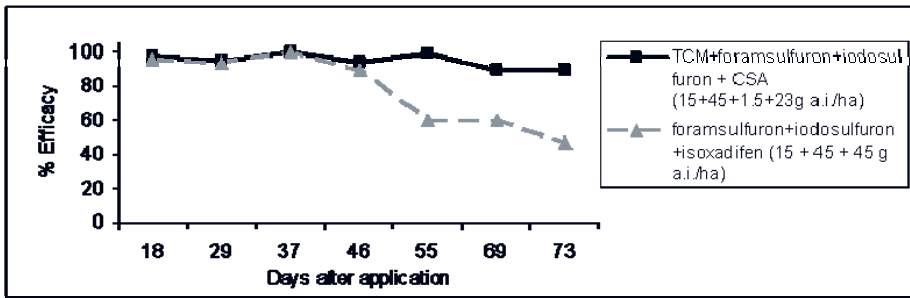
**Fig. 3** Crop tolerance of different herbicide treatments after application at the pre-emergence to early post-emergence (max. 2 leaves of maize) stage of maize. (n) = no. of trials.

**Abb. 3** Die Verträglichkeit verschiedener Herbizidbehandlungen für Mais nach Anwendung im Vorauflauf oder frühen Nachauflauf (max. 2 Blattstadium des Maises) der Kultur. (n) = Anzahl der Versuche.



**Fig. 4** Efficacy of TCM + foramsulfuron + iodosulfuron + CSA (15+45+1.5+23 g a.i./ha) against *Polygonum convolvulus* when applied at different development stages of the weed species. (n) = no. of trials.

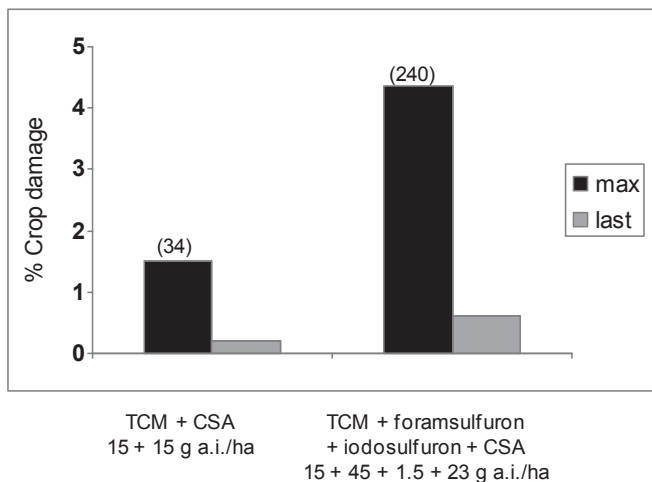
**Abb. 4** Die Wirkung von TCM + Foramsulfuron + Iodosulfuron + CSA (15+45+1.5+23 g a.i./ha) gegen *Polygonum convolvulus* nach Anwendung gegen verschiedene Entwicklungsstadien des Unkrauts. (n) = Anzahl der Versuche.



**Fig. 5** Exemplary demonstration of the residual efficacy of TCM + foramsulfuron + iodosulfuron + CSA against *Chenopodium album* in comparison with foramsulfuron + iodosulfuron + isoxadifen (mean of two trials).

**Abb. 5** Exemplarische Darstellung der Dauerwirkung von TCM + Foramsulfuron + Iodosulfuron + CSA gegen *Chenopodium album* im Vergleich zur Wirkung von Foramsulfuron + Iodosulfuron + Isoxadifen (Mittelwert aus zwei Versuchen).

Crop tolerance of early to mid post-emergent applications of TCM + CSA and also of TCM + foramsulfuron + iodosulfuron + CSA (= Maister power) was well within commercial requirements (Fig. 6). Crop response symptoms included temporary growth retardation and lighter green color of some leaf segments. Maximum damage ratings were taken 10 - 15 days after treatment and stayed on average below 2 % for TCM + CSA and at 4.5 % for its combination with foramsulfuron + iodosulfuron. Final ratings, taken 10 to 11 weeks after application, showed complete recovery of the crop. At any time average crop response ratings stayed below the limit of recognition of crop damage symptoms on a whole field scale.



**Fig. 6** Crop tolerance of different herbicide treatments after application in early to mid- post-emergence (2-6 leaf stage of maize). (n) = no. of trials.

**Abb. 6** Die Verträglichkeit verschiedener Herbizidbehandlungen für Mais nach Anwendung im frühen bis mittleren Nachauflauf (2-6-Blattstadium des Maises). (n) = Anzahl Versuche.

#### 4. Conclusion

TCM, when safened by CSA, is a new useful additional active ingredient for existing maize herbicide solutions. It allows, in combination with the 4-HPPD inhibitors isoxaflutole and tembotrione (SANTEL, 2009) or with the ALS inhibitors foramsulfuron and iodosulfuron, the creation of new broad spectrum herbicides for the selective control of most important annual and perennial grass and dicotyledonous weeds (Tab. 3). Both, combinations of TCM and CSA with isoxaflutole or with foramsulfuron and iodosulfuron result in commercial products, which can offer single pass weed control for a wide range weed infestations and environmental conditions. The soil and foliar activity of TCM not only allows the consistent control of existing weeds but also offers residual control can last for several weeks depending on use rate, soil, and weather conditions. The combination of two different modes of action in one product provides an important element in weed resistance management. The ability of the safener CSA to protect the crop after uptake from the soil or through the leaves secures crop tolerance over the entire use window of TCM ranging from prior to seeding and pre-emergence uses up to the six leaf stage of the target crop maize.

**Tab. 3** Qualitative composition of thien carbazole-methyl-containing commercial corn herbicides.

**Tab. 3** Qualitative Zusammensetzung Thien carbazole-Methyl-haltiger kommerzieller Maisherbizide.

Commercial Product	Active substance					Safener	
	Isoxa-flutole	Thien-carbazone	Foram-sulfuron	Iodo-sulfuron	Tembo-trione	Cypro-sulfamide	Isoxa-difen-ethyl
ADENGO <sup>®</sup> CORVUS <sup>®</sup>	X	X				X	
MAISTER Power <sup>®</sup>		X	X	X		X	
Development product		X	X			X	
CAPRENO <sup>®</sup>		X			X		X

The versatile use characteristics of TCM and CSA allowed to derive an entire family of selective maize herbicides (Tab. 3) from these two new components which have use in conventional maize as well as in herbicide tolerant maize when combined with nonselective herbicides like glyphosate or glufosinate-ammonium (SIMKINS et al., 2009).

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